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VAPOR PHASE REACTIONS OF n-PROPANOL ON SOLID CATALYSTS

by

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A THESIS

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UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Vapor Phase Reactions of n-Propanol on Solid Catalysts" submitted by Kulbhushankumar Vasudeva, in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering.

ABSTRACT

The vapor phase reactions of n-propanol in the presence of solid catalysts were investigated with a view to obtain a catalyst for forming diethyl ketone from n-propanol and to obtain a knowledge about the chemistry of the reactions involved.

Of the two unsupported chromia catalysts obtained by the precipitation of chromia from chromium nitrate solution by sodium hydroxide and ammonium hydroxide respectively the former was found to catalyse the formation of diethyl ketone from n-propanol while the latter resulted primarily in the dehydration of n-propanol. The catalytic activities of three industrial catalyst supports, pumice, polysurface alumina and Norton's alumina were investigated. While the Norton's alumina resulted in the dehydration of n-propanol to propylene and water, the other two materials were found to be inert towards n-propanol. The two supported chromia catalysts obtained by impregnating chromia on the inert supports, pumice and polysurface alumina were found to be active for the decomposition of n-propanol but diethyl ketone was not formed. However, treatment of Norton's alumina with sodium hydroxide solution resulted in a catalyst active for forming diethyl ketone from n-propanol. A base-exchanged

chromia on Norton's alumina was also found to be active for the formation of diethyl ketone from n-propanol.

With the three catalysts, the sodium hydroxide precipitated chromia, the base-exchanged alumina and the base-exchanged chromia on Norton's alumina, active for forming diethyl ketone from n-propanol the highest diethyl ketone yields obtained were 37.6, 42.2 and 48.8 per cent respectively, the corresponding n-propanol conversions being 83.5, 95.8, 100.0 per cent.

The reaction products were identified by a combination of gas phase chromatographic retention time, infrared spectrum and nuclear magnetic resonance spectrum studies. On the basis of the identified products a reaction scheme involving three simultaneous routes, the aldol route, the ester decomposition route involving the regeneration of n-propanol and the ester hydrolysis route, for the formation of diethyl ketone from n-propanol was presented. Experimental runs with propionaldehyde, n-propyl propionate and diethyl ketone as the feeds and a test for the proposed reaction scheme, based on the experimental product distributions obtained with the n-propanol feed and the stoichiometry of the reactions involved, were found to support the proposed reaction scheme.

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The helpful discussion with Dr. D. B. Robinson during the course of the investigation and while preparing the manuscript are gratefully acknowledged.

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I INTRODUCTION

In 1958, one of the large petrochemical firms in Edmonton, Alberta, reported a production of surplus n-propanol and that various means of utilising this surplus were being investigated. One such possibility originated with a publication by Komarewsky and Coley in 1941 (28) in which it was reported that normal alcohols containing n carbon atoms can be converted in the presence of precipitated chromia catalysts to symmetrical ketones containing $2n-1$ carbon atoms. An experimental run using n-propanol as feed was reported to give a diethyl ketone yield of 48.8%.

The possibility of producing diethyl ketone from n-propanol was further explored by Hansen (19) at the University of Alberta. The investigations were carried out in a fluidized bed using alumina supported chromia catalyst. The fluidized bed was chosen in view of its advantages (e.g., nearly constant temperature) for a reaction with significant heat of reaction and the active component, chromia, was supported on alumina to impart to it the mechanical strength desired for fluidized reactors. He obtained a diethyl ketone yield of only 8.7% and concluded that the supported catalyst was inactive for forming diethyl ketone from n-propanol.

Vasudeva (50) investigated the reactions of n-propanol on alumina supported chromia catalyst in a fixed bed and found that the catalyst resulted in the dehydration of n-propanol. Treatment of the catalyst with a sodium hydroxide solution suppressed the dehydration of n-propanol and simultaneously resulted in the formation of diethyl ketone although the diethyl ketone yield was only 15.2%. While the nature of the side reactions was not investigated, it was suggested that the presence of the catalyst support might have been responsible for the low diethyl ketone yield. It was suggested that:

- (a) the reactions of n-propanol be investigated in the presence of unsupported chromia catalyst to determine their extent and nature;
- (b) a catalyst support inactive with respect to n-propanol be sought;
- (c) if diethyl ketone is formed with the unsupported chromia catalyst in yields comparable to those reported by Komarewsky and Coley and if an inactive support is found, a supported chromia catalyst using the inactive support be prepared and its activity be investigated.

The present work was therefore undertaken to investigate the activity of the various chromia catalyst preparations and the chemistry of the reactions involved using n-propanol

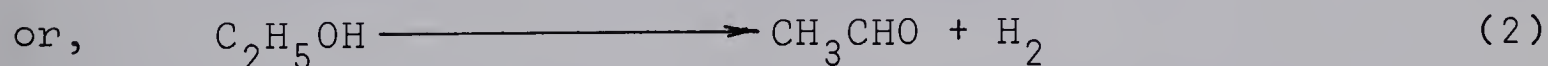
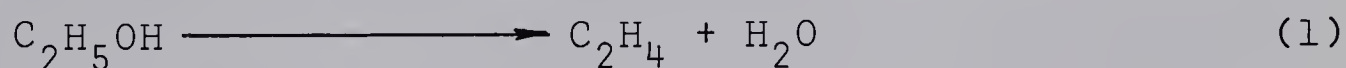
as feed. It was also considered desirable that the diethyl ketone yield of 48.8% be reproduced or improved at space velocities considerably higher than those reported by Komarewsky and Coley.

II LITERATURE SURVEY

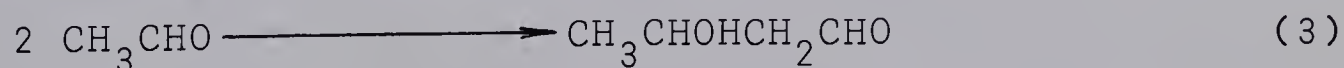
A. Ketones from Primary Alcohols

1. Overall Reactions

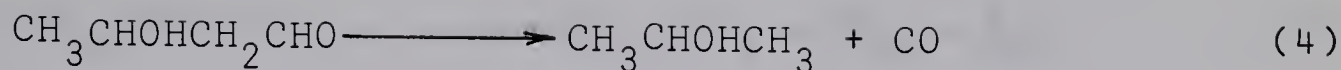
Ipatieff (26) investigated the reactions of ethanol using alumina as a catalyst. An iron tube (480cc capacity) was placed in a high pressure apparatus, charged with 80cc ethanol and 6 gms of alumina, and then heated at 530 - 540°C for 6 hours. During the reaction the pressure reached a maximum of 240 - 260 atmospheres which, after cooling, dropped to 40 - 42 atmospheres. To explain the products of reaction, he suggested that the ethanol decomposes by two different routes.



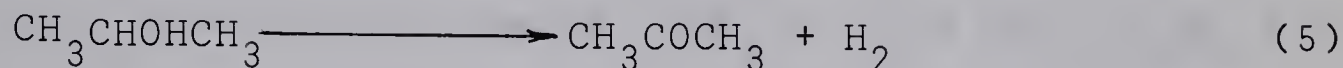
The acetaldehyde formed in reaction (2) may undergo condensation reaction to give acetaldol



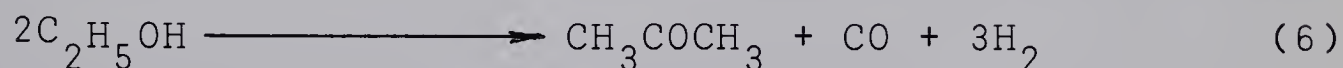
which in turn may decompose like an aldehyde to split off CO



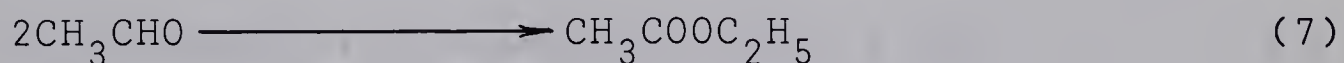
The isopropyl alcohol formed in reaction (4) may then be dehydrogenated to give acetone



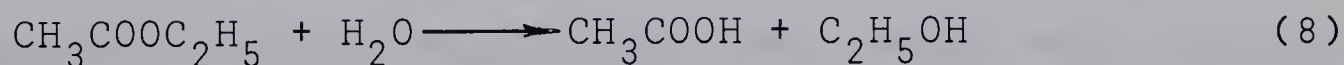
For the aldol route described by reactions (2) to (5) the overall reaction may be written as



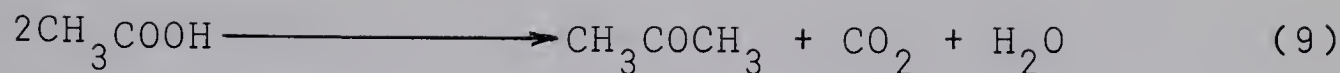
He further suggested that acetone can be formed via an ester route in addition to the aldol route. In the ester route, two molecules of acetaldehyde, formed by reaction (2), combine to give the ester, ethyl acetate,



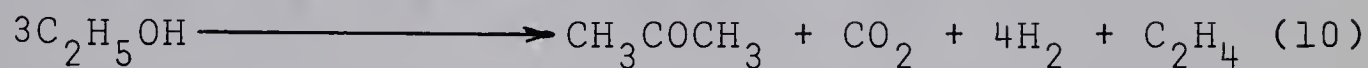
The ester may then be hydrolysed by the water formed by reaction (1)



The acetic acid then reacts to form acetone



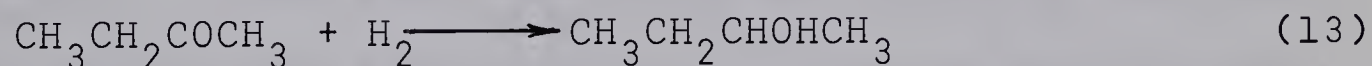
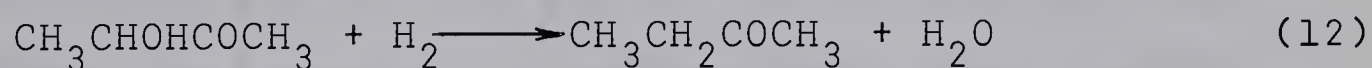
For the ester route, reactions (1), (2) and (7) to (9) the overall equation may be written as



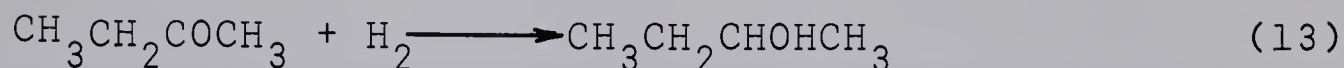
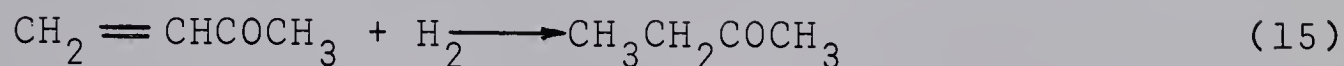
The formation of methyl ethyl ketone and methyl ethyl carbinol, two products which were encountered, was explained by the condensation reaction of acetaldehyde to give the ketol (26)



The ketol may then be reduced in two steps to give methyl ethyl ketone and methyl ethyl carbinol

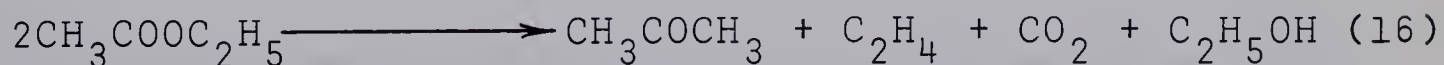


However, a more plausible explanation could be that the formation of methyl ethyl ketone and methyl ethyl carbinol from the ketol takes place by the following reaction sequence,



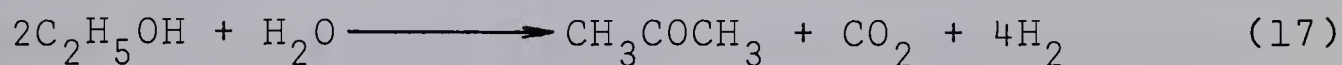
Quantitative yields of the various products were not determined by Ipatieff (26). However, on the basis of gas analyses, he argued that in view of the large amounts of CO_2 produced and the near absence of CO , the formation of acetone takes place predominantly by the ester route.

Kagan et al (27) investigated the mechanism of the formation of acetone from ethanol using copper, oxides of chromium, zinc and their mixtures as catalysts in a flow reactor at atmospheric pressure and a temperature range of 300° to 450°C . Using ethanol, acetaldehyde or ethyl acetate with or without water as feed over these catalysts, they showed that the formation of acetone takes place via the ester route. It was also shown that the ester can decompose directly without any participation of water to give acetone.

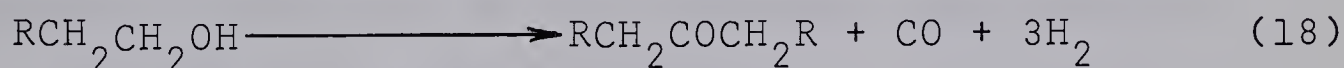


In the absence of water the overall reaction is, therefore, the same as (10). However, if water is added in the feed, the

ester is first hydrolysed and the acid produced then decomposes to give acetone. The overall reaction may be written as



Komarewsky and Coley (28,29) investigated the reactions of normal alcohols, ranging from propyl to octadecyl, using sodium hydroxide precipitated chromia catalysts and reported that normal alcohols containing n carbon atoms can be converted to symmetrical ketones containing $2n-1$ carbon atoms. By passing 4 - 5cc of n -propanol per hour over 119cc of the sodium hydroxide precipitated chromia catalyst at 425°C , they obtained a diethyl ketone yield of 48.8%, unreacted n -propanol being 5.2%. From the analyses of the noncondensable gases they deduced that the reaction takes place via the aldol route, the overall reaction being



The intermediates, aldehydes and aldols, involved in the aldol route were found to yield the corresponding symmetrical ketones.

They also examined the plausibility of the ester route. If the reaction is carried out with an alcohol in which one alpha-hydrogen atom has been replaced by a deuterium atom,

the steps for the aldol and the ester routes are as shown in Figure I. Assuming that the exchange between hydrogen and deuterium is small, the presence of significant amounts of deuterium in the gaseous product may be explained only by the aldol mechanism. Moreover, if the hydrogen and the deuterium atom in the alpha position are equally active, the ratio of hydrogen to deuterium in the gaseous product will be 11:1. In addition, the number of C - D bonds per molecule of ketone equals 2 in the case of the ester mechanism and 1.5 in the case of the aldol mechanism. By using 1-octanol-2-d as feed, they found that their results checked reasonably well with the aldol mechanism thereby providing further support for the aldol route.

2. Individual Reactions

In addition to the above literature on the direct conversion of normal alcohols to the corresponding ketones, the available information on the individual reactions is summarized in the following sections:

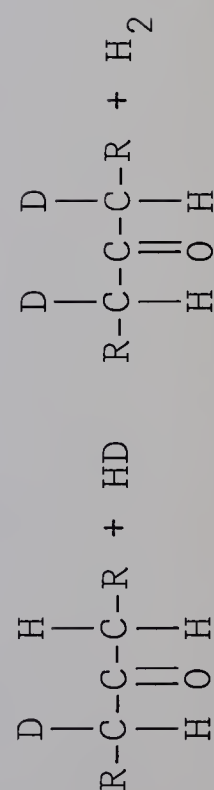
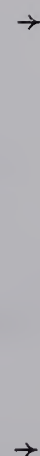
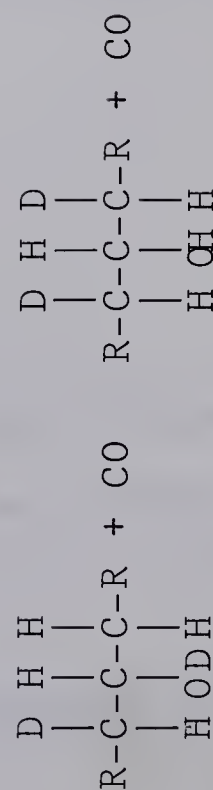
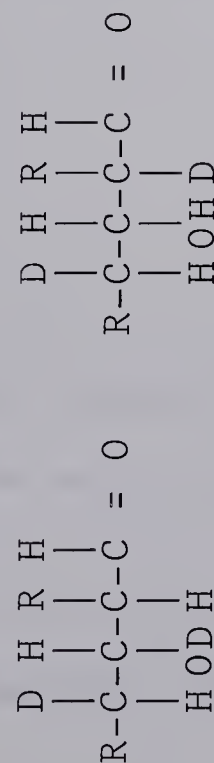
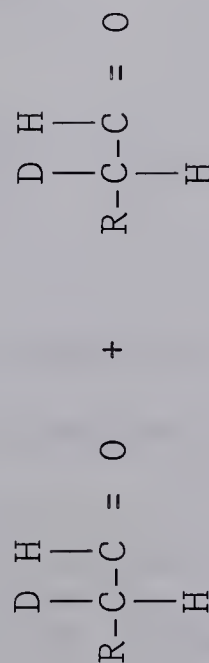
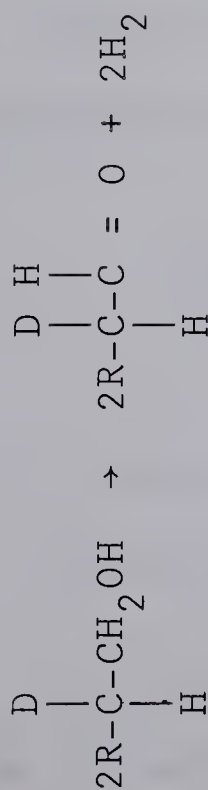
a. Dehydrogenation of Primary Alcohols

Studies on the catalytic dehydrogenation of primary alcohols to yield aldehydes were started by Ipatieff (26) in 1900. Using chromium, manganese, iron, cobalt, nickel, copper, zinc and their oxides, he found that zinc is the best catalyst for the aldehydic decomposition of primary alcohols.

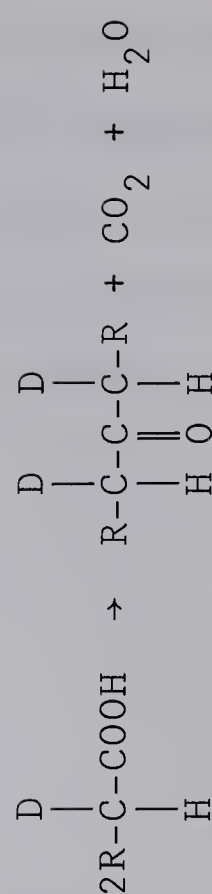
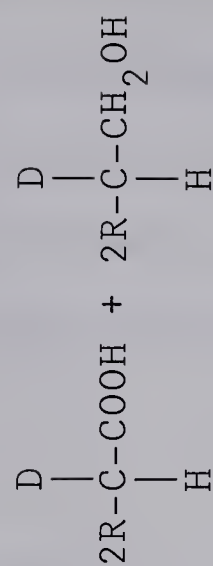
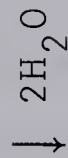
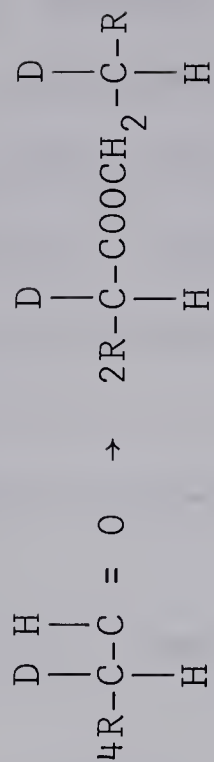
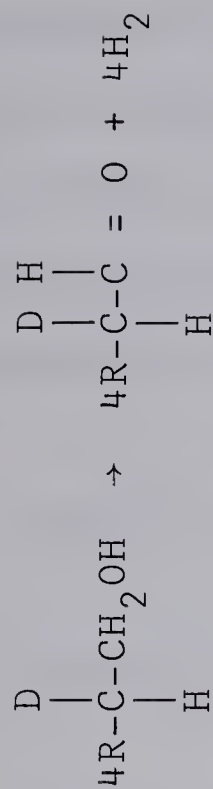
Figure I

REACTION MECHANISM STUDY BY TRACER TECHNIQUE

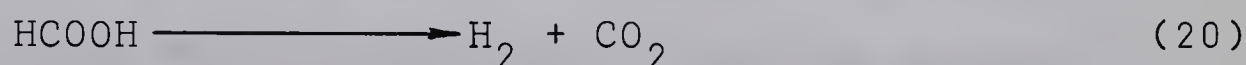
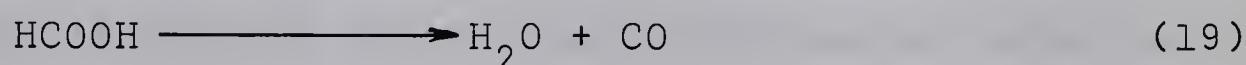
Aldol Mechanism



Cannizzaro or Tischenko Mechanism



In the presence of oxide catalysts, alcohols may undergo dehydration in addition to dehydrogenation depending on the nature of the catalysts. A parallel situation exists in the case of the decomposition of formic acid in the presence of oxide catalysts. Formic acid undergoes dehydration and dehydrogenation as follows:



Mars et al (34) have reviewed the literature on the catalytic decomposition of formic acid. In the case of the decomposition of ethanol in the presence of oxide catalysts it has been observed that a correlation exists between selectivity and the factor η defined as follows:

Selectivity is the ratio of dehydrogenation to total decomposition and

$$\eta = \left(\frac{r_c}{r_a} \right)^3 \frac{1}{Z_c^2}$$

where r_c is the radius of the cation in the catalyst
 r_a is the radius of the anion in the catalyst i.e.,
 oxygen

and Z_c is the valency of the cation.

Thus, in the presence of oxide catalysts, dehydrogenation is

favoured by a large cation radius and a small valency. This is essentially the situation which exists where basicity of the hydroxide is large so that the more basic oxides show a high selectivity for the dehydrogenation reaction. The selectivity, as defined above, decreases in the order MgO , ZnO , Fe_3O_4 , Cr_2O_3 , TiO_2 , SiO_2 and Al_2O_3 ; MgO being essentially dehydrogenating and Al_2O_3 essentially dehydrating. The order of selectivity for the decomposition of formic acid has been found to be the same. In the case of formic acid it has been found that the presence of foreign metallic ions in the catalysts, influences their dehydrogenating activity. Thus, the addition of 5 to 30% potassium carbonate to silica promotes dehydrogenation. Not only potassium ions but also lithium and magnesium ions promote dehydrogenation. On zinc oxide, the addition of alkali (lithium or sodium) increases the rate of dehydrogenation. The mode of action of alkali has not been suggested. While the detailed results are not reported it appears that the presence of alkali increases the rate of dehydrogenation without appreciably influencing the rate of dehydration.

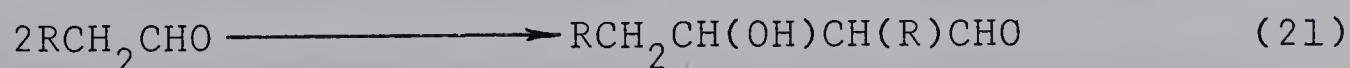
If the similarity between the reactions of formic acid and ethanol, as suggested by Mars et al, exists it can be expected that the presence of alkali in the catalysts would increase the rate of dehydrogenation of ethanol and possibly the other alcohols.

Church and Joshi (10) investigated the dehydrogenation of ethanol using supported and unsupported copper catalysts containing cobalt, chromium, zinc and magnesium oxides as promoters at temperatures of 275 to 350°C. They report that the catalysts containing zinc and magnesium oxides resulted in further condensation of acetaldehyde because of their basic nature. Alumina supported catalysts also resulted in the formation of the aldehyde condensation products and the presence of chromia caused some dehydration. The main by-product, ethyl acetate, was formed to about the same extent with the various catalysts.

Dunbar (14) investigated the dehydrogenation of n-butanol using copper-chromium oxide catalyst supported on pumice, alumina and Celite at temperatures of 330 to 350°C. He reported that in addition to dehydrogenation, dehydration results in amounts that vary with the nature of the support. The aldehyde which is formed further reacts to the ester or to condensation products.

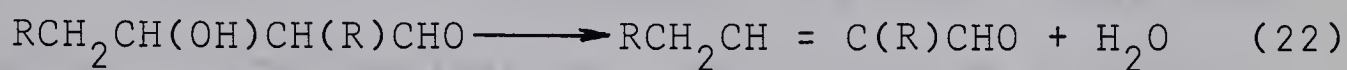
b. Aldol Condensation

Two molecules of an aldehyde containing at least one alpha hydrogen atom may condense to form the aldol



This reaction is catalysed by acids and bases such as hydro-

chloric acid, potassium carbonate, dilute sodium hydroxide, etc., at low temperatures in the liquid phase. When the aldol condensation of an aldehyde is carried out under rather vigorous conditions, e.g., high temperature, and especially when an acid catalyst is used, the reaction tends to proceed to the formation of the α - β unsaturated aldehyde



An important factor tending to limit the yields of simple aldols, or their dehydration products, is the tendency of the condensation product to proceed farther than the dimeric stage giving polyene aldehydes and the cyclic dimer of the aldol (42).

Astle and Zaslowsky (2) investigated the aldol condensation of butyraldehyde using anion exchange resins as catalysts. They report that at low temperatures, below 25°C, the aldol is the main reaction product, while at higher temperatures, the aldol dehydrates to the unsaturated aldehyde. The aldol also dehydrates spontaneously when distilled at atmospheric pressure or when heated with an acid.

Malinowsky and Basinski (32) found that the aldolic reaction between acetaldehyde and formaldehyde in the presence of a silica catalyst treated with sodium hydroxide

solution, at 200 to 350°C gives propenal and water.

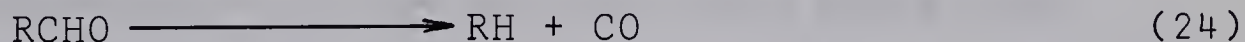


The reaction takes place selectively, the by-products being less than 2%.

Scheidt (43) investigated the vapor phase aldol condensation of propionaldehyde. Using lithium phosphate as catalyst, he obtained 2-methyl-2-pentenal (dehydrated product of propionaldol) with a selectivity of 95%, the conversion being 32% at a temperature of 269-286°C. With calcium hydroxide as a catalyst he obtained a propionaldehyde conversion of 15% at 269-292°C the products being 2-methyl-2-pentenal, 1-propanol and 3-pentanone.

c. Decarbonylation of Aldols

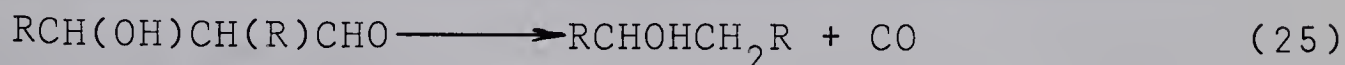
The thermal decomposition of aldehydes to give carbon monoxide and the corresponding hydrocarbon is common to many aldehydes.



Pumice has been found to catalyze this reaction at a temperature of 590-600°C (23). In addition, side reactions, depending on the activity of the hydrocarbon formed, take place. The aldehyde also condenses to give the aldol and

and its dehydration product to some extent.

Ipatieff (26) suggested that the aldol can also undergo this reaction, due to the aldehyde group, to give carbon monoxide and the corresponding secondary alcohol.



Komarewsky and Coley (29) have also presented evidence for the occurrence of this reaction under their reaction conditions, cited earlier.

d. Dehydrogenation of Secondary Alcohols

The catalysts found to be suitable for the dehydrogenation of primary alcohols to aldehydes, described earlier, dehydrogenate secondary alcohols to ketones. It is to be expected that with some catalysts dehydration of the secondary alcohol to give the corresponding unsaturated hydrocarbon will occur. In addition to the dehydration of the secondary alcohol, other reactions may take place due to the activity of the ketone which is produced. However, the aldol condensation of the ketones takes place less readily than that of the aldehydes.

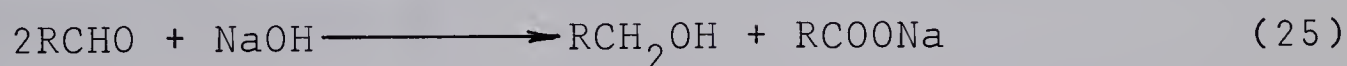
The two catalysts most often referred to for the dehydrogenation of isopropyl alcohol to acetone are copper and zinc oxide. Copper is stated to suffer from the drawback of loss of activity with time and zinc oxide has

some tendency to lead to the dehydration of isopropyl alcohol. In Germany the dehydrogenation was carried out in a stream of hydrogen using zinc oxide as catalyst at 380°C. The catalyst was prepared by heating pumice impregnated with zinc acetate. The isopropyl alcohol conversion is reported to be 98% (15).

The technical C₅ and C₆ normal ketones are obtained from the corresponding secondary alcohols by dehydrogenation over brass catalyst at temperatures 455° to 485°C (15).

e. Tischenko Reaction

Under the influence of a strong aqueous or alcoholic alkali, aldehydes will undergo a disproportionation reaction giving an alcohol and a salt,



This reaction, known as the Cannizzaro reaction, is carried out at room temperature by treatment of the aldehyde with 50% aqueous or alcoholic alkali. The reaction is considered to be characteristic of aliphatic aldehydes in which the alpha-hydrogen atoms are absent, making the aldol condensation structurally impossible. In the case of aliphatic aldehydes possessing alpha-hydrogen atoms, the more rapid aldol condensation occurs on treatment with alkali. However, a

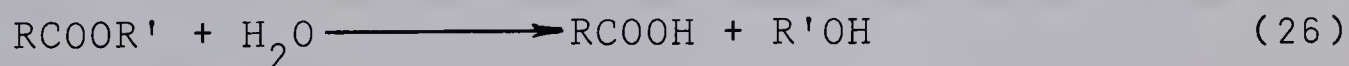
modification of the Cannizzaro reaction, known as the Tischenko reaction, takes place upon treatment of aldehydes with metal alkoxide in non-aqueous media and leads to the formation of the esters.

By using aluminum ethoxide as a catalyst in the inert medium of toluene Child and Adkins (9) obtained ethyl acetate from acetaldehyde. The process has been industrially used in Germany and the overall ethyl acetate yield of 97-98% is reported (15).

Ipatieff (26) and Kagan (27) suggest that the Tischenko reaction takes place in the vapor phase under their reaction conditions, cited earlier.

f. Hydrolysis of Esters .

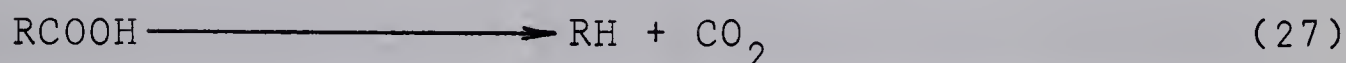
The catalytic hydrolysis of esters in the liquid phase has been the subject of detailed study. The reaction may be written as



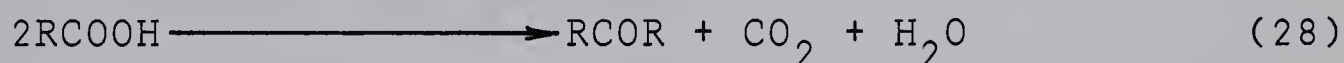
The reaction is catalysed by acids as well as bases and is essentially irreversible in the case of the base catalysis (36). The reaction is also catalysed by cupric ions in the liquid phase (21).

g. Decomposition of Monobasic Aliphatic Acids

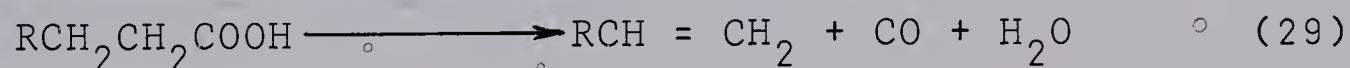
The thermal decomposition of monobasic aliphatic acids results in the formation of CO_2 and the corresponding hydrocarbon



This reaction can be catalysed by the presence of soda lime or sodium hydroxide (24). However, in the presence of metallic oxide catalysts, the acids form the corresponding ketones



Demorest et al (13) studied the catalytic decomposition of acetic, butyric and caprylic acids in the presence of silica, alumina, cracking catalyst and neutralised cracking catalyst. They report that, in addition to the decomposition of the acid to give ketone, another reaction takes place to give carbon monoxide,



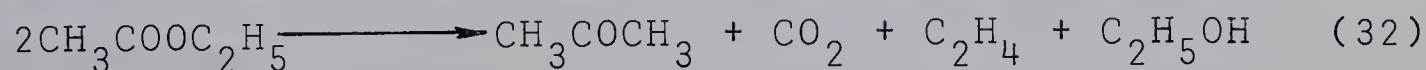
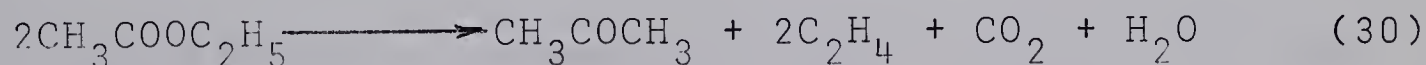
While acetic acid decomposes primarily according to reaction (28), butyric and caprylic acids were found to undergo primarily reaction (29) with silica gel, cracking catalyst

and neutralised cracking catalyst, and reaction (28) with activated alumina.

Ipatieff (26) investigated the catalytic decomposition of acids and found that in the presence of zinc as a catalyst at 590°C, the ketonic decomposition of propionic acid proceeds as readily as that of acetic acid, the chief difference being that propionic acid produces more carbon monoxide and hydrogen. With alumina, thoria and chromia catalysts, ketones are obtained but the yield of ketone drops with rise in molecular weight of the acid.

h. Decomposition of Esters

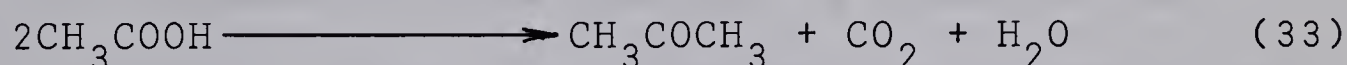
Adkins (1) reports that alumina, titania and thoria at temperatures near 400°C cause ethyl acetate to form varying amounts of ethylene, carbon dioxide, acetic acid, acetone, ethanol and water. The products of reaction may be explained as follows:



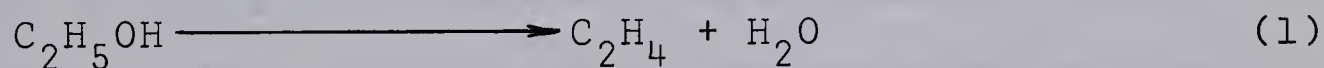
Adkins also found that the type of reaction which a given oxide catalyses is dependent not only on the metallic element

present in the catalyst but also on the method of preparation. By varying the method of preparing aluminas, he showed that the catalytic activity of alumina is conditioned by its molecular porosity or the distances between the aluminum atoms. This in part is determined by the size, shape and position of the radicals attached to the aluminum atom when the aluminum atom goes into solution.

The reactions (30), (31) and (32) may all be primary reactions, occurring under different reaction conditions or to different extents under the same reaction conditions, or consecutive steps involving two reaction schemes may explain the formation of the products of reaction. Thus, reaction (30) may involve the reaction (31) followed by the reaction



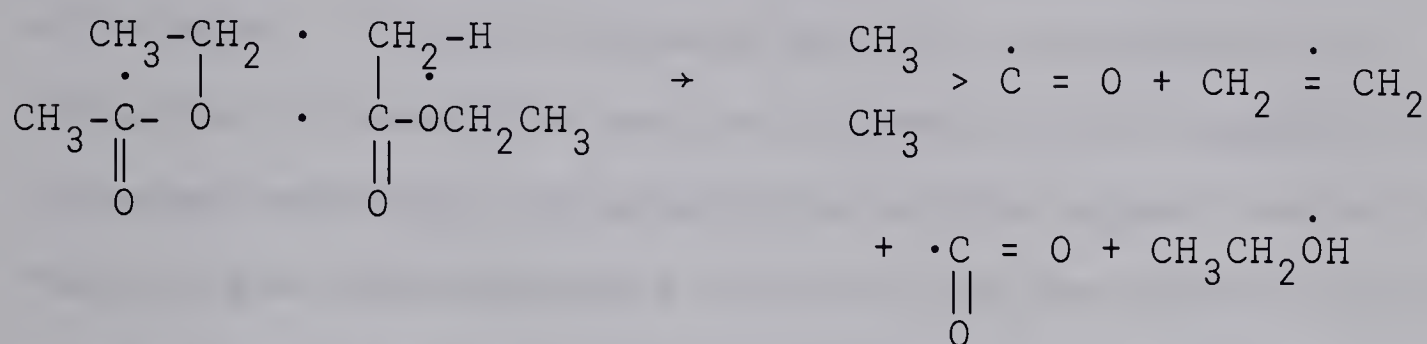
or the reaction (32) followed by the reaction



Evidence for the four-centre-type mechanism reported (22) for the reaction (31) indicates it to be a primary reaction.

The reaction (32) may be explained as the primary reaction, in the presence of heterogeneous catalysts, involv-

ing the adsorption of ethyl acetate on the catalyst at four different points simultaneously, postulated in accordance with Balandin's multiplet theory (47).



B. Solid Catalysts

Most of the contemporary research work on solid catalysts is being carried out to obtain a better understanding on the mechanism of their action. One major approach adopted for fundamental investigations is based on the generally accepted concept that chemisorption of one or more of the reactants by the solid catalysts is a prerequisite for catalytic action. While the nature of the chemisorbed molecules is being investigated by spectroscopic methods (31) it is believed that chemisorption involves electron transfer between the adsorbed molecule and the solid catalyst. This has led to the importance of the electronic character of solids. In case of semi-conductor catalysts attempts are being made to correlate catalytic activity with electrical conductivity and the nature of the semi-conductor (3, 38, 20). Another approach to the electronic character of the solid

catalysts is based on the acid-base character of solids according to the concept of Lewis acidity. Investigations on silica-alumina cracking catalysts (35, 46), alumina (39, 45) and magnesium oxide (33) have been based on the underlying theme of acidity. Another approach made to investigate the mechanism of catalytic action is based on the argument that for some reactions the adsorption of the organic molecule takes place simultaneously on more than one location so that a relationship exists between the dimensions of the organic molecules and the lattice dimensions of the catalyst active for the reaction in question. This is referred to as the geometrical factor (16). Some fundamental work is also being carried out to study the activity of the various catalysts for reactions of simple molecules like ortho-para hydrogen conversion, hydrogen-deuterium exchange, decomposition of formic acid and nitrous oxide, oxidation of carbon monoxide etc.

In addition to the fundamental research on solid catalysts a large amount of work has been carried out to develop and improve catalysts for specific reactions of industrial importance. While most of this information, for commercial reasons, is not published some of it has been compiled as what may be called practical know-how. Thus the type of catalysts for specific reactions, their methods of preparation, the effects of pretreatment on catalytic

activity, physical properties like surface area, pore size distribution, crystal structure determined by x-ray diffraction, effective dispersion of supported catalysts determined by magnetic measurements etc., belong to the realm of practical know-how.

It has, so far, not been possible to formulate any general theories on the basis of fundamental work, that would enable the prediction of a catalyst for a specific reaction. At the same time it has not been possible to put the practical know-how on any fundamental footing with the result that the available information cannot be easily extended to predict the influence of any physical or chemical changes on catalytic activity. This situation of necessity dictates that the development of a catalyst or its improvement be carried out more or less as an art. However, it can be quite helpful in any study of catalytic reactions, undertaken either for purely practical or for scientific purposes, to draw from the practical know-how and scientific results which have been accumulated in this field. The pertinent information on the catalyst systems used in this study has been summarized in the following sections:

1. Chromia as a Catalyst

Chromium, a transition element of the group VIB, acts with oxidation states of +2, +3 and +6. The common oxides of chromium include chromous oxide, CrO ; chromic oxide,

Cr_2O_3 and chromium trioxide, CrO_3 . The oxidation of chromic oxide in air at high temperatures is rather complicated and various oxides intermediate between chromic oxide and chromium trioxide may be obtained. The conditions on the surface of a crystalline or amorphous solid may be different from those prevailing in the bulk phase. Since the catalytic activity has not been associated with any specific oxide the catalyst is generally referred to as chromium oxide or chromia.

Chromia has been found to possess catalytic activity for the following reactions (5):

- (1) Hydrogenation of unsaturated hydrocarbons;
- (2) Dehydrogenation of saturated hydrocarbons;
- (3) Dehydrocyclisation of n-heptane to form toluene;
- (4) Dehydration and dehydrogenation of alcohols;
- (5) Oxidation of carbon monoxide;
- (6) Synthesis of methanol;
- (7) Oxidation of sulfur dioxide to sulfur trioxide;
- (8) Conversion of normal alcohols to ketones.

Chromia catalysts are generally prepared by the following methods (11):

- (1) Decomposition of salts like ammonium dichromate, chromium nitrate and chromium oxalate;
- (2) Precipitation of chromium hydroxide from solutions of soluble salts like chromium nitrate and chromium chloride by alkalies such as sodium hydroxide,

ammonium hydroxide, potassium hydroxide and sodium carbonate;

- (3) Modification of precipitation conditions to form gels;
- (4) Impregnation of a chromium salt solution in a porous support followed by the drying and decomposition of the salt;
- (5) Coprecipitation or cogellation of chromium and aluminum hydroxide from the solutions of the metal salts.

a. Variation of Catalytic Activity with the Nature of Reaction and the Method of Preparation

For the hydrogenation of ethylene the chromia catalyst obtained by precipitation with ammonia is superior to that obtained by the precipitation with alkalies (5). On the other hand, the reverse was found to be true by Komarewsky and Coley (28) for the formation of symmetrical ketones from normal alcohols. They prepared chromia catalysts by four different methods. Their first catalyst was prepared by the precipitation of chromium hydroxide from a cold 1N chromium nitrate solution by 1N sodium hydroxide solution; the second catalyst was made by redissolving the precipitated chromium hydroxide in sodium hydroxide. The chromite solution on standing overnight gave a fine precipitated chromium hydroxide in excess sodium hydroxide; the third catalyst was made by the ignition of chromium nitrate and the fourth catalyst

was obtained by the precipitation of chromium hydroxide gel from a cold 0.1N chromium nitrate solution with a cold 0.1N ammonium hydroxide solution. While the first three catalysts had the same activity for the formation of symmetrical ketones from normal alcohols, referred to as the dehydrogenation-condensation activity, the fourth preparation was comparatively inactive. On the other hand, the relative dehydrocyclisation activity of the four preparations, as determined by the conversion of n-heptane to toluence, was found to be 100%, 7%, 7% and 100% respectively. Thus out of the four catalysts, one catalyses both dehydrogenation-condensation and dehydrocyclisation reactions, two catalyse dehydrogenation-condensation reaction and one catalyses only the dehydrocyclisation reaction suggesting that the activity of a catalyst depends not only on its method of preparation but also on the nature of the reaction to be catalysed.

b. Influence of Temperature on the Activity of
Chromia Catalysts

Lazier and Vaughan (30) studied the catalytic properties of chromium oxide with reference to the hydrogenation of ethylene, dehydrogenation of cyclohexane, dehydrogenation and dehydration of ethanol. A number of preparations using different chromium salts and precipitating agents were investigated. An x-ray examination of the different catalysts showed the amorphous form to be very active as

compared to the practically inactive crystalline form. They also found that the chromia catalysts lose their catalytic activity for the hydrogenation of ethylene on heating to 500°C or higher. This loss of activity is associated with the conversion of the amorphous (and active) chromia to the crystalline (and inactive) form. However, the recrystallisation was found to have little effect on the decomposition of ethanol.

Grosse et al (18) found that pure chromia catalyses the dehydrocyclisation of n-heptane to toluene at 450 to 500°C but loses its activity for dehydrocyclisation at higher temperatures due to recrystallisation.

c. Relationship between the Catalytic Activity and the Electrical Conductivity of Chromia Catalysts

Voltz and Weller (51) investigated the catalytic activity and electrical conductivity of chromia catalysts. The different chromia samples were pretreated with hydrogen or oxygen at 500°C to change their electrical conductivity and their catalytic activity for hydrogen-deuterium exchange was investigated. It was found that as far as the hydrogen-deuterium exchange is concerned chromic oxide has the lowest activity in the state in which it has the greatest number of defects responsible for electrical conductivity. This being contradictory to the predicted effect it was concluded that a simple and direct correlation does not exist between

electrical conductivity and catalytic activity. The catalyst was found to be a p-type semi-conductor.

Griffith and co-workers (7, 8, 17) have published a series of papers on the physical properties of chromium oxide-aluminum oxide catalysts covering the whole range of compositions from pure chromia to pure alumina. They studied surface areas, adsorption characteristics, electrical conductivity, dehydrocyclisation activity and kinetics, structure by x-ray diffraction and magnetic susceptibility. The electrical conductivity varied with the composition of the catalyst by a factor of 1000 while the catalytic activity changed by only a factor of 2. However, no correlation was found to apply over the whole range of compositions. They found that the catalysts reduced in hydrogen at 500°C are n-type semi-conductors if they contain more than 35% chromium oxide. Those with lower chromium content and all mixtures after heating in air are p-type semi-conductors.

The electrical conductivity of semi-conductor oxides can generally be changed by incorporating small amounts of altermvalent ions. If the rate determining steps for the reaction being catalysed involves electron transfer, the rate can be changed by modifying the electrical conductivity of the catalyst. Thus the rate of the hydrogen-deuterium exchange reaction in the presence of zinc oxide catalyst can be increased by incorporating small amounts of oxides of

gallium and aluminum. This is caused by increase of free electrons that results by the addition of an oxide whose cation has a higher valency than zinc. Indeed the addition of lithium oxide to zinc oxide has been observed to decrease the rate of the exchange reaction (20). Zinc oxide is an n-type semi-conductor and its conductivity is associated with free electrons. Chromia has been mentioned by Baker and Jenkins (3) to possess very nearly the properties of an intrinsic semi-conductor though it does show p-type semi-conductivity. While p-type semi-conductivity is associated with electron holes and Hauffe (20) found chromia to be a p-type semi-conductor, he suggested that the production of electron holes is not caused by an excess of oxygen in the oxide lattice so that its electrical conductivity cannot be changed by the addition of foreign oxides with cations of different valencies.

Thus there is no clear cut agreement between the various workers about the type of conductivity associated with chromia catalysts and the various attempts made to correlate the catalytic activity and the electrical conductivity of chromia catalysts have not met any success.

2. Alumina as a Catalyst

Pure, nearly anhydrous alumina is known to occur in several distinct crystalline modifications. Stumpf et al (45) have studied the thermal transformations of aluminas

and aluminum hydrates. The seven crystalline modifications of the nearly anhydrous aluminas obtained by heating pure alumina hydrates were called α -, γ -, δ -, η -, κ -, θ - and χ -alumina. Four hydrates, namely α - and β - monohydrate and α - and β - trihydrate were studied. The basic sequences of transformations occurring on heating to various temperatures have been reported. Milliken et al (35) report that the alumina structure may involve four or six co-ordinated aluminum atoms and that the various crystal forms are arrangements involving one or both of the co-ordination states of aluminum.

Alumina possess the ability to catalyse reactions such as polymerisation, isomerisation, cracking and alkylation of hydrocarbons and dehydration of alcohols. Since these reactions are also catalysed by strong acids in the liquid phase, the catalytic activity of alumina has been associated with its acid centres. Pines and co-workers (39) studied the chemisorption of trimethylamine and adsorption of various indicators on alumina and have shown it to possess intrinsic acidity.

The literature reveals striking discrepancies with respect to the catalytic activity of aluminas. To cite a few examples (39), the dehydration of primary alcohols such as 1-butanol in the presence of alumina is reported by many authors to give pure 1-olefin whereas others have found mixtures

of double bond isomers. Further, some workers report that olefins undergo only a double bond shift while others have observed a skeletal rearrangement. This suggests that all aluminas do not possess the same type of catalytic activity. Pines et al (39) found that there are two aspects of acidity - qualitative, involving the number of acid sites, and quantitative, involving the strength of acid sites and that not all aluminas give the same picture of acidity. Certain reactions such as the isomerization of cyclohexane are catalysed by only strong acids whereas reactions like the dehydration by 1-butanol is caused by both strong and weak acids. Heating the alumina catalysts to temperatures higher than 700°C decreased the number of acid sites as well as their acid strength. Treatment of alumina with ammonia from the gas phase resulted (40) in preferential poisoning of the strong acid sites. However, dehydration of alcohols was found to take place. It was suggested that the carbonium ion character of dehydration is suppressed by treatment with ammonia and the reaction takes place by a concerted mechanism involving both acid and basic sites present on the surface of alumina. Impregnation of pure alumina with sodium hydroxide (39) was found to lead to a partial poisoning of the active sites without appreciably altering the strength of the remaining sites. With increasing amounts of alkali, a parallel decrease for cyclohexane isomerization, butanol dehydration and amine

chemisorption was observed.

Oblad et al (37) report that alumina is an amphoteric substance and may have the properties of an acid or a base depending upon its environment and that in a four-coordinated state it acts as an acid. On the other hand, Webb (52) suggests that the acidity of alumina probably arises from the three-coordinated aluminum atom; also in the dehydrated state the defect sites are acids only in the Lewis sense but when hydrated they are Bronsted acids. Tung et al (48) have shown that high purity alumina possesses fairly good activity for butene-1 isomerization but relatively poor activity for propylene polymerization at 195°C and for cumene cracking and hexene cracking below 400°C. Above 400°C, high purity alumina has good cracking activity. The results are explained by assuming alumina to possess Lewis acid sites and passive Bronsted acid sites. They also found that alumina generates more hydrogen gas in its cracked product as compared to silica-alumina. This is suggested to be due to the presence of the dehydrogenation centres on the alumina surface.

3. Use of Catalyst Support

Most commercial catalysts consist primarily of one or more active constituents supported or deposited on an 'inert' material called the catalyst carrier or support. The desirable effects which a support imparts to the catalyst may be one or more of the following (6, 25):

- (1) Giving a larger exposed surface of the active component and thereby a greater catalytic activity per unit weight of the active component in cases where the latter by itself has a low surface area;
- (2) Increasing the catalyst stability by keeping the fine crystals of the active constituent too far apart for sintering to occur;
- (3) Modifying favorably the catalytic activity or selectivity, poison resistance, etc., of the active constituent;
- (4) Helping to dissipate heat and prevent local overheating which could cause sintering and the resultant loss of active surface;
- (5) Imparting mechanical strength to the catalyst. This is particularly important in industrial operations from the point of view of materials handling. In operations involving large heat effects a fluidized bed is very desirable for which attrition resistance is required;
- (6) Pore size distribution has been postulated to have an important influence on selectivity. Since the pore size distribution of the supported catalyst probably depends on that of the support, the latter may have a very strong influence on the selectivity of the supported catalyst.

The activity and selectivity of a catalyst, supported

or unsupported, depend on its chemical as well as physical properties. The presence of a support may influence both physical and chemical properties thereby influencing its activity and/or selectivity. To cite a few examples, Berkman (6) reports that zinc oxide is known to be a specific dehydrogenating catalyst giving an aldehydic decomposition of ethyl alcohol. However, this aldehyde type of reaction can be converted into the ethylene type (dehydration) by supporting zinc oxide on a charcoal support which by itself is inactive towards alcohol. Selwood and co-workers (44) showed that for manganese oxide supported on alumina, manganese was tetravalent at high concentrations, at low concentrations it adopted the structure of the alumina support and was trivalent whereas at intermediate concentrations the average valency was between three and four. When manganese ions are present in both +3 and +4 valency states electron transfer both to and from the catalyst is facilitated, resulting in an increase in the activity of the catalyst for reactions where the rate controlling step involves electron transfer.

The typical examples, cited above, indicate that even an inactive support may have a very strong influence on the activity of the catalyst. However, the manner in which a support interacts with the active component is not well understood. This makes the choice of a catalyst support extremely difficult, essentially a trial-and-error procedure.

While there is no restriction on the type of materials which can be used as catalyst supports, the ones most commonly used in industrial practice are alumina, silica gel, activated carbon, pumice, asbestos, kieselguhr and magnesia. Silica gel and most aluminas are obtained by chemical methods starting with the chemically pure compounds while the others are generally obtained from naturally occurring materials. Some aluminas are obtained by directly heating natural bauxite and they will contain impurities. In addition to their use as catalyst supports alumina, silica and magnesia are also used as catalysts and co-catalysts.

4. Supported Chromia Catalysts

As already pointed out there is no restriction on the types of material which can be used as catalyst supports. However, the studies reported in the literature are restricted primarily to alumina supported chromia catalysts. The salient features brought out by these studies are briefly described below.

Griffith and co-workers (7) prepared co-precipitated chromia-alumina catalysts and found that the surface area increases with increasing alumina content.

Grosse et al (18) found that pure chromia produces dehydrocyclisation of n-heptane to toluene at 450 to 500°C but rapidly loses activity on heating to higher temperatures. This loss of activity is associated with the recrystallisation

of chromia. It was found that the active life of the catalyst can be extended to over 1000 hours by supporting the catalyst on alumina.

The results of Voltz and Weller (51) indicate that chromia is about three times more efficiently distributed in the alumina supported chromia catalyst than in the unsupported chromia catalyst.

A better picture of chromia-alumina catalyst has emerged since the investigations of Selwood and co-workers (44). They investigated a number of catalyst preparations of chromium content varying from 0.1 to 40% prepared by impregnation of chromic acid solutions on high surface area γ -alumina followed by drying, ignition and reduction with hydrogen. Chromia-alumina catalysts prepared by co-precipitation were also studied for comparison. The investigations included surface area measurements, magnetic susceptibility measurements, x-ray diffraction studies and catalytic activity for the dehydrocyclisation of n-heptane. The interpretation of the experimental results pointed out the following conclusions:

- (1) The surface area per gram of alumina decreases with increasing chromium concentration. At a chromium concentration of 30% the surface area was only 70% of that for pure alumina per gram of alumina.
- (2) Even at chromium concentrations too low to form a

monomolecular layer on alumina surface, the small portion of alumina covered has chromia in the form of very small, widely scattered, microcrystalline particles.

- (3) Effective dispersion of chromia decreases with increase in concentration but increases with hot impregnation.
- (4) Gross changes in carrier area have a large influence on the effective dispersion of chromia provided the measurements are being made in a region where most of the surface is covered.
- (5) Prolonged heating in air to 600°C caused a small loss in activity. Chromia probably slowly dissolves in the support but the loss of activity is not caused by any aggregation or growth of chromia microcrystals.
- (6) In the co-precipitation series the chromia particles varied in size from substantially isolated chromium ions to macrocrystals.

The literature cited above is typical and points out the difficulties encountered in drawing any specific conclusions regarding the exact influence of, say, the method of catalyst preparation, or the presence of catalyst support or any other foreign material. The exact source of catalytic activity, in general, is not known. Until a better understanding is obtained of the mechanism of catalytic action the development of catalysts has to be carried out specifically for every case.

The general conclusions may be summarized as follows:

- (1) Chromia catalysts of widely varying activity may be obtained depending on the method of preparation.
- (2) A certain chromia catalyst may be active only for a specific reaction while another chromia preparation may be required for another reaction.
- (3) Certain chromia catalysts have a moderate activity for converting n-propanol to diethyl ketone.
- (4) Chromia catalyst is in general active in the amorphous form and may lose activity on crystallisation.
- (5) The active life of chromia catalysts can be extended by the use of a suitable support.
- (6) Certain alumina preparations have the catalytic activity typical of acids. In addition to the acid sites, pure alumina also possesses dehydrogenation sites.
- (7) The catalytic activity of alumina, associated with the acid sites, can be suppressed by treatment with an alkaline solution such as sodium hydroxide.
- (8) Use of γ -alumina as a support for chromia catalysts results in an increased dispersion of chromia.
- (9) Catalyst supports may have a very strong influence on the activity of the active component even though the support, by itself, is inactive.

III EXPERIMENTAL PROCEDURES

A. Catalyst Preparation

The catalytic activity and selectivity of a catalyst preparation depends on its chemical and physical characteristics which in turn are influenced by the method of preparation. An almost unlimited range and number of variables like the nature of the starting salt of the active component, concentration of solutions, temperature, nature of precipitating agent, nature of catalyst support, conditions during drying and decomposition, any subsequent treatment etc., make the total number of possible methods of catalyst preparation very large. Since the effect of these factors is, in general, unknown it becomes necessary to select the method of catalyst preparation more or less arbitrarily.

The methods used for catalysts preparation during this study are briefly described below. The detailed methods and the materials used are included in Appendix II.

1. Unsupported Chromia Catalysts

a. Sodium Hydroxide Precipitated Chromia

Chromium oxide was precipitated by neutralising a cold 1N chromium nitrate solution by a cold 1N sodium hydroxide solution. The precipitate was filtered, dried and

reduced with n-propanol.

b. Ammonium Hydroxide Precipitated Chromia Gel

The precipitation of chromium oxide from a chromium nitrate solution with ammonium hydroxide solution was carried out under conditions such that instantaneous precipitation was avoided by adding ammonium acetate to the chromium nitrate solution. The delayed precipitation, after all the ammonium hydroxide had been added, resulted in the setting of the whole mass in the form of a gel. The gel was washed, dried and reduced with n-propanol.

2. Catalyst Supports

a. Norton's Alumina

1/8" x 1/8" Norton's alumina cylinders as supplied were crushed and screend. The -10+20 mesh fraction was used for the present study.

b. Polysurface Alumina

Polysurface alumina (-2+4 mesh) as supplied by Carborundum Co. was crushed, screened and the -10+20 mesh fraction was used for the present study.

c. Pumice

Pumice stone, -8+14 mesh, as supplied was used.

3. Pretreated Norton's Alumina

a. Norton's Alumina heated to 1200°C

The -10+20 mesh fraction obtained after crushing and screening was heated at 1200°C in air for 1 hour.

b. Base-exchanged Norton's Alumina

The -10+20 mesh Norton's alumina fraction was immersed in a 2N sodium hydroxide solution for 6 hours. The excess solution was drained and the solids were dried.

4. Supported Chromia Catalysts

Chromia on pumice and polysurface alumina were obtained by impregnation from a 2N chromium nitrate solution, draining off the excess solution, drying the solids and decomposing the nitrate retained in the pores, by heating to 400°C. The decomposed catalyst was reduced with n-propanol.

For treating chromia on pumice with sodium hydroxide, the reduced chromia on pumice was immersed in a 2N solution of sodium hydroxide, the excess solution was drained off and the solids were dried.

5. Base-exchanged Chromia on Norton's Alumina

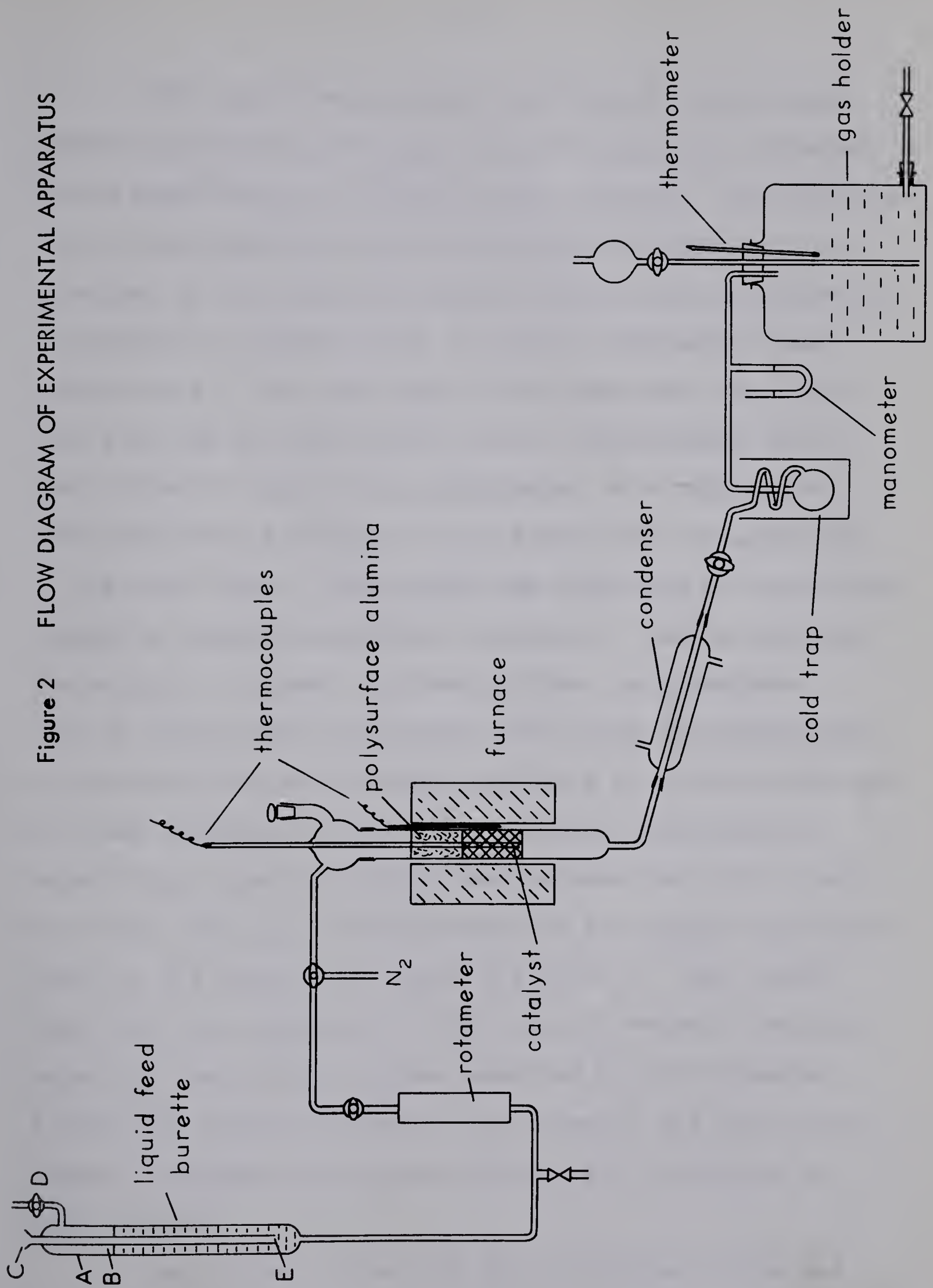
Chromia on Norton's alumina was obtained by impregnation from 2N chromium nitrate solution, followed by drying, decomposing and reducing the oxide. The reduced catalyst was immersed in a 2N sodium hydroxide solution for 6 hours. The excess solution was drained off and the solids were dried.

B. Determination of the Activity of the Catalysts

1. Experimental Apparatus

A flow diagram of the experimental apparatus used in this study is shown in Figure 2. The apparatus consisted of a vertical pyrex glass reactor 22 millimeter outside diameter and 45 centimeter long. A porous quartz disc provided to support the catalyst charge rested on four small recesses made into the reactor at 28 centimeters from the top of the reactor. A reactor head consisting of an inlet for charging the catalyst, another inlet for the liquid feed and a four-hole quartz tube connected the reactor to the liquid feed system. Through the quartz tube pass two 28 gauge chromel wires and two 28 gauge alumel wires to form two thermocouples 10 centimeters apart enabling two temperatures to be measured inside the reactor. The thermocouple wires were connected, through a multipoint selector switch, to a Leeds and Northrup potentiometer. The top of the four-hole quartz tube was sealed with a sealing wax. The reactor was heated by a 30 centimeter long, 3.2 centimeter inside diameter hinged type heavy duty electric furnace controlled by a powerstat. A chromel-alumel thermocouple located half-way along the length of the furnace was used to measure the temperature between the furnace and the reactor. The gap between the furnace and the reactor at both the ends was plugged by 1/8 inch asbestos string to minimize the temperature gradient along the furnace.

Figure 2 FLOW DIAGRAM OF EXPERIMENTAL APPARATUS



The liquid feed system consisted of a calibrated burette specially constructed so as to maintain a constant liquid head during the course of the reaction. The construction of the calibrated burette is shown in Figure 2. It consisted of two concentric glass tubes A and B, 2.0 and 0.4 centimeters in diameter and 45 and 42 centimeters long respectively. The outer tube A was blown onto the inner tube B at the top end and the inner tube extended into a small funnel C open to the atmosphere. A 4 millimeter glass tube with a stopcock D was blown into the upper end of the outer tube. The burette was connected to the reactor through a Matheson laboratory rotameter. During operation the stopcock D closed the burette from the atmosphere. Flow of liquid from the burette took place by displacement of air which entered through the tube B so that the pressure at E was atmospheric during the course of the reaction permitting a constant liquid head between the point E and any other point at the downstream end as long as the liquid level in the burette was above the point E. The liquid feed rate was controlled by the stopcock between the rotameter and the reactor and was measured by the rotameter. A three-way stopcock between the rotameter and the reactor enabled nitrogen to be passed through the reactor as and when required.

The product condensing and collecting system was

connected at the downstream end of the reactor as shown in Figure 2. It consisted of a 15 centimeter long glass condenser cooled by passing water at room temperature. The cooled reaction products passed into a liquid product receiver which consisted of a glass coil having a 100 cc bulb at the bottom and a side outlet to drain the collected product. The liquid product receiver was cooled by ice-water mixture contained in a Dewar flask. A three-way stopcock provided between the condenser and the liquid product receiver enabled the liquid product to be collected in a separate receiver and the gas product to be vented to the atmosphere during the unsteady state period of the experimental run. During the steady state period the liquid product could be collected in the cold trap and the non-condensable gases were collected over a saturated sodium chloride solution in a calibrated gas holder provided with a thermometer and manometer.

2. Operating Procedure

The reactor was positioned in the furnace so that a 10 centimeter long catalyst bed would occupy the central 10 centimeter length of the furnace leaving a 10 centimeter heated section of the furnace on either side of the catalyst bed. The porous quartz disc used to support the catalyst bed was placed in its position. The reactor head was fitted into the top of the reactor so that the thermocouples were in place. A known weight of the catalyst was then charged into

the reactor so that it occupied nearly 10 centimeter length of the reactor. Sufficient amount of polysurface alumina (-6+10 mesh) was charged to form an 11 centimeter long bed above the catalyst. This acted as a preheater zone to vaporize and preheat the feed to the reaction temperature. The furnace was switched on and the temperature of the reaction zone brought up to the desired level by adjusting the powerstat while passing nitrogen through the reactor bed. Once the desired temperature was reached the nitrogen flow rate was discontinued and the liquid feed started at a predetermined rate. During the initial period of the run the temperature of the catalyst bed changed and by adjusting the furnace current was brought back to the desired level. This period was considered the unsteady state period and the products of reaction were not collected. Once the temperature level at a point was nearly constant (1°C) and the liquid feed rate was constant the run was continued for 1 to 1-1/2 hours depending on the liquid feed rate. The products were collected during this period. At the end of the run the product collection system was disconnected, the liquid feed stopped, the furnace turned off and the catalyst bed allowed to cool while passing nitrogen through it. The difference between the initial and the final level of liquid in the calibrated burette gave the amount of the liquid feed. The liquid product was drained from the liquid product

receiver and weighed. The volume, temperature and pressure of the gas collected were noted.

C. Identification of Products

Identification of reaction products was carried out by one or more of the following methods:

- (a) Study of the retention times in gas-solid and gas-liquid chromatography
- (b) Infra-red spectroscopy
- (c) Nuclear Magnetic Resonance spectroscopy

The experimental details are as follows:

1. Liquid Product

The components of the liquid product were separated by gas-liquid chromatography using a Burrell Model KD Kromotog. After trying a number of column packings and various operating conditions it was found possible to carry out the separation by using a Ucon on Celite column. The experimental conditions used were as follows:

Column: 1/4 inch diameter 16 foot long column made into a spiral and packed with 30% Ucon on Celite. Ucon, designated as Ucon Lubricant LB-1800X was supplied by Union Carbide Chem. Co.

Column Temperature: 100°C for the first twelve minutes followed by a 10°C/min temperature rise to a temperature of 150°C.

Carrier Gas : Helium

Gas flow rate : Carrier side - 60 cc/min.

Reference side - 30 cc/min.

For preliminary identification of the compound in question, the retention time in the column was used. A sample of the reaction product was chromatographed. A small amount of the suspected compound was mixed with a sample of the reaction product and chromatographed again under the same conditions as used for the reaction product. If the peak of the substance in question increased, in comparison with the other peaks, a tentative identification of the compound in question was considered as established.

To confirm the identification of the compound in question, by infra-red and nuclear magnetic resonance spectroscopy, it was isolated in pure form by the following method:

A sample of the reaction product was injected into the chromatographic column. The effluent from the Kromotog was led to bubble through spectroscopic grade carbon tetrachloride contained in a 2 cc vial during the time when the peak of the compound in question was being recorded on the chart. The compound in question was retained by carbon tetrachloride and the carrier gas escaped. If the peak corresponding to the compound to be trapped immediately followed another peak, the trapping was started about 15

seconds after the first peak ended so as to allow for the travel of the component from the thermal conductivity cell to the effluent end. With the small diameter column that could be used in the laboratory chromatograph it was found that to get a good separation of some of the compounds their amounts in the injected sample should be only 1-2 μ l. This made it necessary to trap the component in question from a large number of injections to get a reasonable amount (20-30 μ l) of the isolated compound for identification by spectroscopy.

The infra-red spectra of the isolated compounds were obtained on Perkin Elmer's Model 401 Infra-Red Spectrometer and were interpreted to identify the structural units in the compounds under question.

The nuclear magnetic resonance spectra of the isolated compounds were obtained on Varian Associates HR 100 NMR Spectrometer and were interpreted to identify the compounds.

2. Gas Product

The components of the gas product were separated by chromatography by using two columns. The experimental conditions used were as follows:

(1) Column : 30% Ucon on Celite (same as
for the liquid product)

Column Temperature: Room

Carrier Gas : Helium

Gas Flow Rate : Carrier side 20 cc/min.

Reference side 30 cc/min.

Components Separated: Carbon dioxide and propylene

(2) Column : 1/16 inch diameter, 8 foot long
activated charcoal column made
into a spiral.

Column Temperature : Room

Carrier Gas : Helium

Gas Flow Rate : Carrier side 40 cc/min.

Reference side 30 cc/min.

Components Separated: Hydrogen, oxygen, nitrogen and
carbon monoxide.

Identification of the gaseous components was carried out by checking the retention times of the unknown components with those of the pure samples of the suspected components.

D. Analysis of Products

1. Liquid Product

The quantitative analyses of the liquid products were carried out by vapor phase chromatography using a 30% Ucon on Celite column under the conditions already described in the section on the identification of products. The analyses were based on calibrations obtained with synthetic mixtures of compositions very near to those of the unknown products

and were carried out as follows:

A 4 μ l sample of the unknown product was chromatographed and its composition was estimated by using the relationship

Per cent by weight of the component A

$$= \frac{\text{peak area for the component A} \times 100}{\text{Sum of the peak areas for all the components separated}}$$

The peak areas were determined by multiplying the height of the peak by the width of the peak at half the height.

A synthetic mixture of composition very nearly the same as estimated above was prepared from pure samples of the major identified products and a 4 μ l sample of the synthetic mixture was chromatographed under conditions same as those used for the unknown sample. The quantitative analysis of the unknown sample was then calculated by comparing the chromatograms for the unknown and the synthetic samples and using the relationship:

Per cent by weight of A in the unknown sample

Per cent by weight of A in the synthetic mixture

$$= \frac{\text{Peak area for A in the unknown sample}}{\text{Peak area for A in the synthetic sample}}$$

The components analysed by this method were propionaldehyde,

methyl ethyl ketone, n-propanol, diethyl ketone, n-propyl propionate and 3-pentanol. Since pure samples were not available for ethyl isopropyl ketone, 2-methyl-2-pentenal and 3-octanone their amounts in the liquid products were evaluated by comparing their areas with those for methyl ethyl ketone or diethyl ketone whichever was present in comparable amounts in the sample being analysed.

2. Gas Product

The quantitative analysis of the gas product was carried out by gas chromatography using two different columns. Hydrogen and carbon monoxide were separated and analysed by using activated charcoal column while Ucon on Celite column was used for carbon dioxide and propylene. The experimental conditions used for separation have already been described in the section on the identification of products.

For quantitative analysis synthetic mixtures of known compositions were prepared from air and each of the gases, hydrogen, carbon monoxide, carbon dioxide and propylene, present in the reaction product. A known volume of each of the synthetic mixtures was chromatographed using the respective columns under the experimental conditions used for analysis and calibration curves were obtained by plotting peak area versus per cent composition for carbon monoxide, carbon dioxide and propylene. The peak areas were obtained

by multiplying the peak height by the width of the peak at half the height. Since helium was used as the carrier gas the signal recorded on the chart for hydrogen, when its content in the mixture was more than 50% consisted essentially of two peaks i.e., before the pen came back to the base line another peak was recorded so that the peak area for hydrogen could not be found out. Therefore, the calibration curve for hydrogen was plotted as the total length of the path traced by the pen versus the per cent hydrogen in the gas mixture.

For analysing the unknown gas product, a known volume of the gas sample, same as that used for calibration, was chromatographed in each of the columns. The total length of the path traced for the hydrogen signal and the peak areas for carbon monoxide, carbon dioxide and propylene were determined and the per cent of these gases in the product were found out from the calibration curves.

IV EXPERIMENTAL PROGRAM AND RESULTS

A. Catalytic Activity

1. Activity of the Unsupported Chromia Catalysts

The low diethyl ketone yields, 8.7% and 15.2%, reported by Hansen (19) and Vasudeva (50) respectively using alumina supported chromia catalysts as compared to the high diethyl ketone yield, 48.8%, reported by Komarewsky and Coley (28) using sodium hydroxide precipitated chromia catalyst suggested that the activity of the latter catalyst be reinvestigated.

The sodium hydroxide precipitated chromia catalyst was prepared by Komarewsky and Coley's method (28). The experimental conditions, temperature and space velocity, used to evaluate its catalytic activity are given in Table I.

The temperature was measured at two points, 4 inches apart, along the length of the catalyst bed. During the course of the reaction the temperature at either point varied by less than $\pm 1^{\circ}\text{C}$ but there was an appreciable temperature gradient along the catalyst bed. The reported temperature is the arithmetic average for the two points along with the maximum deviation for each run.

The space velocity as reported is defined as

Table I

ACTIVITY OF UNSUPPORTED CHROMIA CATALYSTS

Operating Conditions and Material Accountability

Run No.	Catalyst	Catalyst Charge gms.	Temp. °C	Space Velocity hr ⁻¹	Liquid Feed gms.	Liquid Product gms.	Gas Product gm.moles	Material Accountability %
1	Sodium Hydroxide Precipitated Chromia	14.0	405±14	0.62	13.1	12.0	0.060	94.6
2	Sodium Hydroxide Precipitated Chromia	14.0	479±16	0.57	11.9	7.7	0.292	87.3
3	Ammonium Hydroxide Precipitated Chromia gel	20.0	403±10	0.39	11.8	7.4	0.190	94.3

$$\text{Space velocity} = \frac{\text{Liquid feed rate in gms/hr}}{\text{Weight of the catalyst in gms}}$$

and its units are hr^{-1} .

A measure of the efficiency with which the reaction products are collected is reported in Table I as the per cent material accountability and has been defined as

% Material Accountability

$$= \frac{\text{Weight of the liquid product} + \text{Weight of the gas product}}{\text{Weight of the liquid feed}} \times 100$$

The weight of the liquid feed is known from the initial and the final level in the calibrated liquid feed burette. The liquid product collected was weighed. Knowing the volume, the temperature and the pressure of the gas product the number of moles of gas was calculated by using the ideal gas law. To calculate the weight of the gas from the number of moles and the gas analysis, the experimental gas analysis, reported in Table II, was corrected so that the total assay of the gases added up to 100%.

The analyses of the gas and the liquid products are given in Table II. The experimental method for the analysis has already been explained in the section on analysis of products.

The product distributions reported as moles of each of the identified products per mole of the n-propanol feed

Table II

ACTIVITY OF UNSUPPORTED CHROMIA CATALYSTS

Analysis of Products

Run No.	1	2	3*
Liquid Analysis, per cent by weight			
Propionaldehyde	6.1	18.9	19.2
Methyl Ethyl Ketone	Tr	3.6	1.8
n-Propanol	82.5	21.7	16.4
Diethyl Ketone	1.9	29.4	5.8
Ethyl Isopropyl Ketone	Tr	1.0	8.2
3-Pentanol	Tr	0.5	Tr
n-Propyl Propionate	3.0	2.1	13.6
2-Methyl-2-Pentenal	Tr	1.0	2.1
3-Octanone	<u>Tr</u>	<u>1.8</u>	<u>1.9</u>
Total	93.5	81.0	69.0
Gas Analysis, per cent by volume			
Hydrogen	87.0	74.4	59.0
Carbon Monoxide	1.7	9.0	0.8
Carbon Dioxide	7.8	8.7	5.9
Propylene	<u>1.7</u>	<u>2.3</u>	<u>36.5</u>
Total	98.2	94.4	102.2

* Analysis of non-aqueous layer

are given in Table III. The liquid product collection system suffers from the disadvantage that some of the liquid product may be retained in the condenser and the liquid product receiver and may not be recovered for weighing resulting in less than 100% material accountability. Since the gas volume was measured very accurately the weight of the gas was considered accurate and the uncertainty in the quantitative collection of the liquid product for weighing was overcome by calculating its weight by subtracting the weight of the gas from that of the feed. Using the calculated liquid product and the liquid product analysis, the moles of the various identified products per mole of the n-propanol feed have been calculated.

The % n-propanol conversions and the % diethyl ketone yields reported in Table III have been defined as follows

% n-propanol conversion = $100 \left(\frac{\text{moles of n-PrOH in the product}}{\text{per mole of n-PrOH in the feed}} \right)$

% diethyl ketone yield

$$= \frac{2 \times \text{moles of DEK in the product/mole of n-PrOH in the feed}}{\% \text{ n-PrOH conversion}} \times 100$$

where n-PrOH is n-propanol

and DEK is diethyl ketone

The precipitation of chromia by sodium hydroxide

Table III
ACTIVITY OF UNSUPPORTED CHROMIA CATALYSTS

Product Distribution

Moles per Mole of n-Propanol Feed

Run No.	1	2	3
Liquid			
Propionaldehyde	0.0616	0.1500	0.1117
Methyl Ethyl Ketone	Tr	0.0229	0.0084
n-Propanol	0.8000	0.1650	0.0922
Diethyl Ketone	0.0128	0.1570	0.0228
Ethyl Isopropyl Ketone	Tr	0.0044	0.0277
3-Pentanol	Tr	0.0027	Tr
n-Propyl Propionate	0.0151	0.0083	0.0398
2-Methyl-2-Pentenal	Tr	0.0044	0.0072
3-Octanone	Tr	0.0066	0.0050
Gas			
Hydrogen	0.244	1.160	0.555
Carbon Monoxide	0.005	0.140	0.008
Carbon Dioxide	0.022	0.135	0.056
Propylene	0.005	0.036	0.343
% n-Propanol Conversion	20.0	83.5	90.8
% Diethyl Ketone Yield	12.8	37.6	5.0

resulted in a very voluminous precipitate which was difficult to filter. In industrial operations such gelatinous precipitate offer inherent disadvantages such as the difficulty of washing and filtering. However, if the precipitation is carried out under conditions that lead to gel formation, trapping all the water in the structure of the precipitate, the need for filtration is avoided and the specific activity of the catalyst, in general, remains unchanged. Keeping this in view a chromia gel catalyst was prepared. However, the conditions required for the gel formation are very specific and have to be followed very accurately. The procedure described by Turkevich et al (49), involving the precipitation with ammonium hydroxide, was used and the results obtained with this catalyst are reported, along the same lines as those for the sodium hydroxide precipitated chromia catalyst, in the Tables I, II and III. However, in the case of the chromia gel the liquid product separated into two layers - the upper organic layer and the lower aqueous layer. It was not found possible to analyse the aqueous layer by vapor phase chromatography and hence the results reported are based on the organic layer only.

2. Activity of the Catalyst Supports

The sodium hydroxide precipitated chromia catalyst was found to be active for converting n-propanol to diethyl ketone but did not possess physical stability under the

reaction conditions. It was, therefore, decided to investigate the possibility of obtaining a supported chromia catalyst that possessed adequate catalytic activity and physical stability under the reaction conditions. While the catalytic activities of the support and the active component may not be additive it is desirable that the catalyst support, by itself, does not possess any activity that may lower the yield of the required product. The criteria for the suitability of the catalyst support were therefore chosen as the physical stability under the reaction conditions and the inability to catalyze any reactions that may lower the yield of diethyl ketone.

The catalytic activity of three industrial catalyst supports, Norton's alumina, polysurface alumina and pumice, for the decomposition of n-propanol was investigated to examine their suitability as catalyst supports for the present study. The chemical composition and the physical properties of these materials are included in the Appendix I. The operating conditions and the material accountabilities for the experimental runs 4 to 7 are reported in Table IV on the same basis as those reported in Table I. The quantitative analysis of the reaction products was not carried out but a qualitative examination of the liquid products from runs 4 to 6 by vapor phase chromatography showed them to be essentially n-propanol except for trace quantities of propionaldehyde in

Table IV

ACTIVITY OF CATALYST SUPPORTS

Operating Conditions and Material Accountability

Run No.	Catalyst	Catalyst Charge gms.	Temp. °C	Space Velocity hr ⁻¹	Liquid Feed gms.	Liquid Product gms.	Gas Product gm. moles	Material Accountability %
4	Empty Reactor	-	427±7	a	11.7	11.40	1.91x10 ⁻³	97.5*
5	Polysurface Alumina	37.0	438±1	0.24	11.0	10.9	4.53x10 ⁻³	98.5*
6	Pumice	17.0	455±1	0.51	10.8	10.4	6.33x10 ⁻³	95.9*
7	Norton's Alumina	25.0	355±6	0.58	16.5	4.4	0.2465	89.6

* Weight of gas neglected.

a Liquid feed rate = 11.7 gms/hr

the case of runs 5 and 6. In the case of run 7, the liquid product was found to be essentially water and the gas product was propylene.

3. Activity of Pretreated Norton's Alumina

Norton's alumina was found to be unsuitable for supporting chromia for the present study as it catalysed the dehydration of n-propanol. The attempts made to suppress the dehydrating activity of Norton's alumina were pursued along two lines:

(a) heating Norton's alumina to 1200 °C,

(b) treating Norton's alumina with sodium hydroxide solution.

The operating conditions used to determine the catalytic activity of the two pretreated aluminas are reported in Table V along with the material accountabilities obtained. The gas analysis, the moles of gas product per mole of the n-propanol feed and the nature of the reactions are reported in Table VI. The analysis of the liquid product from run 10 is reported in Table VIII.

4. Activity of the Supported Chromia Catalysts

The relative inertness of pumice and polysurface alumina with respect to n-propanol, reported in Table IV, suggested that they may be of interest for supporting chromia catalysts for the present study.

The supported chromia catalysts, using pumice and

Table V

ACTIVITY OF PRETREATED NORTON'S ALUMINA

Operating Conditions and Material Accountability

Run No.	Catalyst	Catalyst Charge gms.	Temp. °C	Space Velocity hr ⁻¹	Liquid Feed gms.	Liquid Product gms.	Gas Product gm.moles	Material Accountability %
7	Norton's Alumina	25.0	355±6	0.58	16.5	4.4	0.2465	89.6
8	Norton's Alumina Heated to 1200°C	22.5	467±4	0.39	13.1	4.7	0.200	89.7
9	Base-exchanged Norton's Alumina	22.5	352±8	0.56	9.9	9.5	0.006	95.8*
10	Base-exchanged Norton's Alumina	22.5	461±1	0.40	13.0	7.0	0.357	84.6

* Weight of gas neglected.

Table VI

ACTIVITY OF PRETREATED NORTON'S ALUMINA

Gas Analysis and Nature of Reaction

Run No.	Gas Analysis			% Vol.	Gas Produce Moles per Mole of n-Propanol Feed	Nature of Reaction
	H ₂	CO	CO ₂	C ₃ H ₆		
7	-	-	-	99.0	0.896	Dehydration of n-propanol
8	16.0	0.8	6.5	69.0	0.916	Dehydration of n-propanol and formation of diethyl ketone
9	not analysed				0.036	Not known
10	73.8	11.5	12.0	2.9	1.646	Formation of diethyl ketone

polysurface alumina as supports, were prepared by the methods already described and their catalytic activity was evaluated. The experimental conditions and the results are reported in Tables VII, VIII and IX.

The possible promoting influence of sodium on the activity of chromia as suggested by Coley et al (12) was examined by preparing a sodium hydroxide treated chromia on pumice catalyst. The results for its activity are also reported in the Tables VII, VIII and IX.

The three supported catalysts, chromia on pumice, chromia on polysurface alumina and the sodium hydroxide treated chromia on pumice were found to be inactive for forming diethyl ketone from n-propanol. On the other hand the base-exchanged Norton's alumina was found to catalyse the formation of diethyl ketone from n-propanol. Any possible improvement in the diethyl ketone yield obtained with the base-exchanged Norton's alumina as a catalyst by using a combination of chromia and the base-exchanged Norton's alumina was examined by preparing the base-exchanged chromia on Norton's alumina. The experimental conditions used to determine its catalytic activity and the results obtained are reported in the Tables VII, VIII and IX. The experimental results for run 10 using the base-exchanged Norton's alumina are also reported in Table IX.

The influence of temperature on the activity of the

Table VII

ACTIVITY OF SUPPORTED CHROMIA CATALYSTS

Operating Conditions and Material Accountability

Run No.	Catalyst	Catalyst Charge gms.	Temp. °C	Space Velocity hr ⁻¹	Liquid Feed gms.	Liquid Product gms.	Gas Product gm.moles	Material Accountability %
11	Chromia on Pumice	18.0	451±8	0.49	13.5	11.0	0.088	92.5
12	NaOH Treated Chromia on Pumice	18.0	455±6	0.53	11.7	10.3	0.028	96.2
13	Chromia on Polysurface Alumina	37.0	450±11	0.32	13.8	10.6	0.087	85.3
14	Chromia on Polysurface Alumina	37.0	478±11	0.33	11.9	8.5	0.116	86.4
17	Base-exchanged Chromia on Norton's Alumina	22.5	467±2	0.37	9.0	5.0	0.295	89.1

Table VIII

ACTIVITY OF SUPPORTED CHROMIA CATALYSTS

Analysis of Products

Run No.	11	12	13	14	17	10
Liquid Product, per cent by weight						
Propionaldehyde	21.5	3.7	15.6	25.6	1.6	1.7
Methyl Ethyl Ketone	-	-	-	-	3.8	3.1
n-Propanol	73.6	89.3	72.3	57.8	1.3	6.0
Diethyl Ketone	-	-	-	-	53.7	41.8
Ethyl Isopropyl Ketone	-	-	-	-	5.4	4.1
3-Pentanol	-	-	-	-	1.1	1.6
n-Propyl Propionate	-	-	1.5	1.9	0.4	Tr
2-Methyl-2-Pentenal	-	-	-	-	Tr	Tr
3-Octanone	-	-	-	-	6.5	5.0
Total	95.1	93.0	89.4	85.3	73.8	63.3
Gas Product, per cent by volume						
Hydrogen	59.5	21.6	66.9	65.6	75.2	73.8
Carbon Monoxide	0.6	0.5	0.5	1.9	12.6	11.5
Carbon Dioxide	2.2	3.0	4.4	9.0	11.9	12.0
Propylene	<u>30.1</u>	<u>71.0</u>	<u>23.2</u>	<u>21.1</u>	<u>2.4</u>	<u>2.9</u>
Total	92.4	96.1	95.0	97.6	102.1	100.2

Table IX
ACTIVITY OF SUPPORTED CHROMIA CATALYSTS

Product Distribution

Moles per Mole of n-Propanol Feed

Run No.	11	12	13	14	17	10
Liquid						
Propionaldehyde	0.1990	0.0352	0.1472	0.2260	0.0101	0.0118
Methyl Ethyl Ketone	-	-	-	-	0.0200	0.0180
n-Propanol	0.6570	0.8200	0.6610	0.4940	0.0077	0.0415
Diethyl Ketone	-	-	-	-	0.2360	0.202
Ethyl Isopropyl Ketone	-	-	-	-	0.0200	0.0169
3-Pentanol	-	-	-	-	0.0046	0.0065
n-Propyl Propionate	-	-	0.0072	0.0084	0.0013	Tr
2-Methyl-2-Pentenal	-	-	-	-	Tr	Tr
3-Octanone	-	-	-	-	0.0133	0.0164
Gas						
Hydrogen	0.252	0.0328	0.264	0.393	1.470	1.21
Carbon Monoxide	0.002	0.0007	0.0019	0.0109	0.245	0.189
Carbon Dioxide	0.009	0.0045	0.0172	0.0540	0.231	0.197
Propylene	0.128	0.1080	0.0914	0.1262	0.047	0.047
% n-Propanol Conversion	34.3	18.0	33.9	50.6	99.2	95.8
% Diethyl Ketone Yield	0.0	0.0	0.0	0.0	47.6	42.2

base exchanged chromia on Norton's alumina was investigated and the experimental conditions and results are reported in the Tables X, XI and XII.

B. Identification of the Reaction Products

The major constituents in the reaction products obtained in various runs were identified by the methods already described in the section on experimental procedures, to enable a quantitative analysis of the reaction products. A knowledge of the reaction products can also be used to suggest a reaction scheme to explain the formation of the various products. The products which were separated and identified and the methods used for their identification are reported in Table XIII.

C. Chemistry of the Reactions of n-Propanol

A reaction scheme, proposed on the basis of the identified products, involved propionaldehyde and n-propyl propionate as intermediates for the formation of diethyl ketone from n-propanol. The product distributions obtained with the three catalysts active for the formation of diethyl ketone from n-propanol were found to be similar suggesting that the same reaction sequence was followed with each of the catalysts. To lend further evidence to the proposed reaction scheme experimental runs were carried out with propionaldehyde and n-propyl propionate as feeds using the base-exchanged chromia on Norton's alumina catalyst. The

Table X

ACTIVITY OF BASE-EXCHANGED CHROMIA ON NORTON'S ALUMINA

Operating Conditions and Material Accountability

Run No.	Temp. °C	Space Velocity hr-l	Liquid Feed gms.	Liquid Product gms.	Gas Product gm.moles	Material Accountability
15	403±10	0.38	12.1	10.4	0.094	92.0
16	446±6	0.37	11.7	8.1	0.280	91.8
17	467±2	0.37	9.0	5.3	0.300	95.5
18	479±2	0.38	9.0	5.0	0.295	89.1

Table XI

ACTIVITY OF BASE-EXCHANGED CHROMIA ON NORTON'S ALUMINA

Product Analysis

Run No.	15	16	17	18
Liquid Product, per cent by weight				
Propionaldehyde	17.5	12.1	1.6	1.0
Methyl Ethyl Ketone	Tr	1.4	3.8	6.4
n-Propanol	66.4	19.4	1.3	Tr
Diethyl Ketone	3.3	26.4	53.7	49.1
Ethyl Isopropyl Ketone	Tr	2.4	5.4	7.3
3-Pentanol	Tr	0.8	1.1	1.0
n-Propyl Propionate	2.2	0.7	0.4	0.6
2-Methyl-2-Pentenal	1.1	3.0	Tr	Tr
3-Octanone	<u>0.5</u>	<u>5.3</u>	<u>6.5</u>	<u>4.4</u>
Total	91.0	71.5	73.8	69.8
Gas Product, per cent by volume				
Hydrogen	81.0	77.0	75.2	68.5
Carbon Monoxide	3.2	8.7	12.6	9.7
Carbon Dioxide	7.5	10.3	11.9	9.7
Propylene	<u>5.0</u>	<u>2.0</u>	<u>2.4</u>	<u>2.0</u>
Total	96.7	99.0	102.1	89.7

Table XII

ACTIVITY OF BASE-EXCHANGED CHROMIA ON NORTON'S ALUMINA

Product Distribution

Moles per Mole of n-Propanol Feed

Run No.	15	16	17	18
Liquid				
Propionaldehyde	0.1700	0.0972	0.0101	0.0063
Methyl Ethyl Ketone	0.0014	0.0092	0.0200	0.0348
n-Propanol	0.6220	0.1510	0.0077	Tr
Diethyl Ketone	0.0153	0.1430	0.2360	0.2440
Ethyl Isopropyl Ketone	0.0009	0.0112	0.0200	0.0288
3-Pentanol	Tr	0.0041	0.0046	0.0042
n-Propyl Propionate	0.0106	0.0027	0.0013	0.0018
2-Methyl-2-Pentenal	0.0061	0.0142	Tr	Tr
3-Octanone	0.0023	0.0191	0.0192	0.0133
Gas				
Hydrogen	0.391	1.120	1.470	1.500
Carbon Monoxide	0.015	0.123	0.245	0.213
Carbon Dioxide	0.035	0.147	0.231	0.213
Propylene	0.024	0.025	0.047	0.040
% n-Propanol Conversion	37.8	84.9	99.2	100.0
% Diethyl Ketone Yield	8.1	33.7	47.6	48.8

Table XIII
LIST OF IDENTIFIED PRODUCTS

No.	Name of Product	Chemical Formula	Means of Identification*	IR	NMR
1	n-Propanol	C_3H_7OH	x	x	x
2	Propionaldehyde	C_2H_5CHO	x	x	x
3	2-Methyl-2-Pentenal	$C_2H_5CH=C(CH_3)CHO$		x	x
4	3-Pentanol	$C_2H_5CHOHC_2H_5$	x		
5	Diethyl Ketone	$C_2H_5COC_2H_5$	x	x	x
6	n-Propyl Propionate	$C_2H_5COOC_3H_7$	x	x	
7	Water	H_2O	x		
8	Methyl Ethyl Ketone	$CH_3COC_2H_5$	x	x	x
9	Ethyl Isopropyl Ketone	$CH_3CH(CH_3)COC_2H_5$		x	x
10	3-Octanone	$C_5H_{11}COC_2H_5$		x	x

Gas products, H_2 , CO , CO_2 and C_3H_6 identified by GPC

- * GPC = gas phase chromatographic retention time
IR = infra-red spectroscopy
NMR = nuclear magnetic resonance spectroscopy

experimental conditions and the results for these runs are reported in Tables XIV, XV and XVI. The stability of diethyl ketone under the reaction conditions was examined by using diethyl ketone as the feed and the results are included in the Tables XIV to XVI.

Table XIV

SPECIAL TEST USING PROPIONALDEHYDE, n-PROPYL PROPIONATE
AND DIETHYL KETONE FEEDS

Operating Conditions and Material Accountability

Catalyst - Base-Exchanged Chromia on Norton's Alumina

Run No.	Liquid Feed	Temp. °C	Space Velocity hr-1	Liquid Feed gms.	Liquid Product gms.	Gas Product gm.moles	Material Accountability %	- 77 -
19	Propionaldehyde	418±15	1.33	11.0	8.6	0.0305	83.6	
20	Propionaldehyde	457±21	0.32	7.1	3.5	0.107	77.0	
21	n-Propyl Propionate	456±8	0.40	7.5	4.3	0.116	84.4	
22	Diethyl Ketone	467±11	0.43	9.6	8.7	0.0187	95.4	

Table XV

SPECIAL TESTS USING PROPIONALDEHYDE, n-PROPYL PROPIONATE
AND DIETHYL KETONE FEEDS

Analysis of Products

Run No.	19	20	21	22
Liquid Product, per cent by weight				
Propionaldehyde	77.1	1.4	1.8	0.6
Methyl Ethyl Ketone	Tr	2.8	2.7	4.2
n-Propanol	0.9	Tr	1.0	-
Diethyl Ketone	5.5	44.1	53.6	82.5
Ethyl Isopropyl Ketone	Tr	2.5	3.1	2.7
3-Pentanol	Tr	0.6	0.6	0.5
n-Propyl Propionate	Tr	Tr	0.5	-
2-Methyl-2-Pentenal	8.8	Tr	Tr	-
3-Octanone	<u>Tr</u>	<u>4.6</u>	<u>2.4</u>	<u>-</u>
Total	92.3	56.0	64.9	90.5
Gas Product, per cent by volume				
Hydrogen	57.1	74.4	46.3	50.4
Carbon Monoxide	7.0	9.0	21.4	5.7
Carbon Dioxide	35.5	8.7	11.9	42.1
Popylene	<u>1.8</u>	<u>2.3</u>	<u>6.0</u>	<u>1.9</u>
Total	101.4	94.4	85.6	100.1

Table XVI

SPECIAL TESTS USING PROPIONALDEHYDE, n-PROPYL PROPIONATE
AND DIETHYL KETONE AS FEEDS

Product Distribution

Moles per Mole of Feed

Run No.	19	20	21	22
Liquid				
Propionaldehyde	0.7310	0.0099	0.0256	0.0078
Methyl Ethyl Ketone	Tr	0.0162	0.0316	0.0482
n-Propanol	0.0081	Tr	0.0142	-
Diethyl Ketone	0.0351	0.2150	0.5270	0.7890
Ethyl Isopropyl Ketone	Tr	0.0106	0.0261	0.0221
3-Pentanol	Tr	0.0029	0.0061	0.0041
n-Propyl Propionate	Tr	Tr	0.0033	-
2-Methyl-2-Pentenal	0.0416	Tr	Tr	-
3-Octanone	Tr	0.0150	0.0161	-
Gas				
Hydrogen	0.0904	0.476	0.978	0.0850
Carbon Monoxide	0.0110	0.116	0.452	0.0096
Carbon Dioxide	0.0564	0.256	0.186	0.0708
Propylene	0.0029	0.014	0.127	0.0032

V INTERPRETATION AND DISCUSSION OF RESULTS

In a catalytic system, if a number of simultaneous and consecutive reactions are possible, the reactions catalysed depend on the catalyst used. A knowledge of the chemistry of the different reactions catalysed is, therefore, necessary to enable a meaningful comparison of the activity of the various catalysts. In the following sections the chemistry of the reactions involved will therefore be discussed first and then the activity of the catalysts will be discussed in the light of the reactions involved.

A. Chemistry of the Reactions of n-Propanol

The approach adopted to obtain a knowledge of the chemistry of the reactions involved consisted essentially in identifying the stable compounds in the reaction product and postulating a reaction sequence on the basis of the identified products. Supporting evidence for the postulated reaction sequence was obtained by experimental runs with the reaction intermediates.

The products identified during the course of the experimental work and the methods used for identification were shown in Table XIII. The validity of the methods of identification may be examined as under:

a. Identification by Gas Chromatography

Identification of products by gas chromatography is based on the fact that the relative retention volumes for a particular type of compounds, say, ketones, vary with the size of the molecule and are reproducible under similar conditions of apparatus assembly (4). However, the calculation of relative retention volume is unnecessary for identification since the time required for the elution of a compound, called the retention time, is constant when the separation is carried out under fixed conditions of column size, shape and temperature and carrier gas flow rate. A comparison of retention time of the unknown compound and that of a pure sample of the suspected compound, therefore, gives a good preliminary identification of the compound in question.

However, gas chromatography as an identification method has two limitations. First, some idea of the nature of the compound in question is required to enable a check of its retention time with reference samples. Second, two compounds belonging to different classes may have the same retention time in a column packed with a particular stationary phase. The second limitation makes gas chromatography a technique which is only useful for tentative identification.

b. Identification by Infra-Red Spectroscopy

The infra-red spectrum of a compound gives information as to the presence or absence of various functional

groups in the compound e.g., hydroxyl group, carbonyl group, ester group, unsaturation, etc. However, for an easy interpretation of the spectrum for identification purposes the sample should contain only one compound.

The compounds separated by gas chromatography were isolated by the method already explained in the section on experimental methods. An examination of the infra-red spectrum then gives information on the type of compound and can generally indicate the presence of more than one types of compounds in the sample. Therefore, an examination of the infra-red spectra of the compounds isolated by gas chromatography overcomes both the limitations of gas chromatography as a tool for identification. The types of compounds expected in the reaction product in the present study are primarily oxygenated compounds like alcohols, aldehydes, ketones, esters, ethers and some hydrocarbons. Except for the presence of hydrocarbons in samples of the other components the rest can be very readily distinguished by infra-red spectroscopy. Since no high molecular weight hydrocarbons can be expected in the reaction product, this was not considered as any limitation in the present study.

Of the eight compounds whose IR spectra were studied only five were confirmed by retention time study because pure reference samples were not available for the others. Since IR spectra by themselves give information only

on the type of compound, a complete identification requires use of some additional means of identification.

c. Identification by Nuclear Magnetic Resonance Spectroscopy

The proton magnetic resonance spectroscopy (a special case of NMR spectroscopy) can be used to locate the position of the various hydrogen atoms in an organic molecule with respect to each other. The position of the proton signals in the applied field depends on the electronic environment around the proton. The presence of any substituent group in the molecule, therefore, introduces a chemical shift. The availability of characteristic proton chemical shifts, for protons directly bonded to the substituent group and for those not directly bonded to the substituent group, as standard information for many compounds enables a very reliable identification of the compound in question. In combination with IR spectra, the NMR spectra are therefore accepted to conclusively establish the identity of the compounds in question.

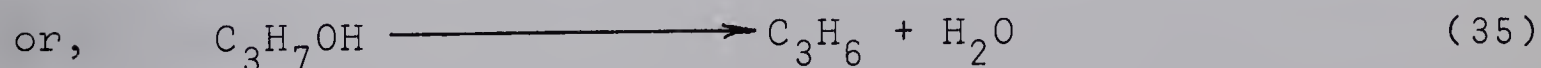
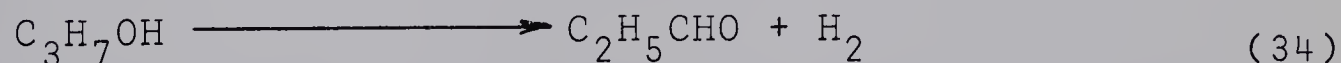
A reference to Table XIII therefore shows that the identity of n-propanol, propionaldehyde, diethyl ketone, 2-methyl-2-pentenal, methyl ethyl ketone, ethyl isopropyl ketone and 3-octanone is conclusively established. The small amount of 3-pentanol formed in the reaction product made it very difficult to isolate enough sample for obtaining its IR and NMR spectra and the evidence offered by gas chroma-

tography may be accepted as adequate. The n-propyl propionate was identified by gas chromatography and IR spectroscopy which give adequate confirmation of its presence in the liquid product. The identification of water, when formed, did not offer any difficulty because it separates as an aqueous phase. Moreover, when chromatographed it gives a peak which tails very strongly and under the chromatographic conditions was found to be typical of water only.

The identification of the gaseous components by gas chromatography has been accepted as adequate.

A postulated reaction scheme, based primarily on these identified products and that explains the formation of the various products, particularly those involved in the formation of diethyl ketone, is shown in Figure 3. The compatibility of this reaction scheme with the experimental observations will now be shown.

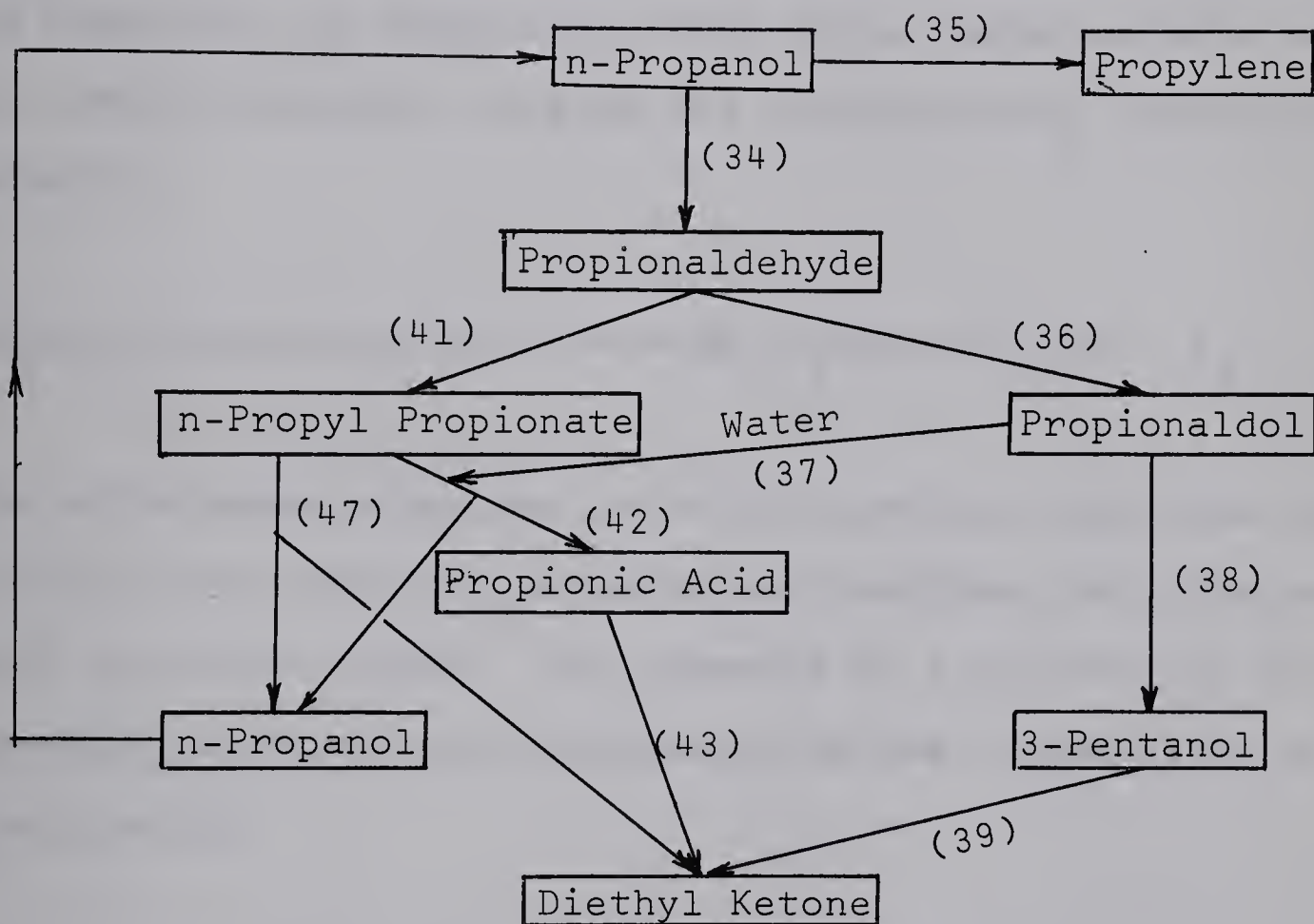
The n-propanol is dehydrogenated to propionaldehyde or dehydrated to propylene,



The four products, namely propionaldehyde, hydrogen, propylene and water have been identified in the reaction product. The

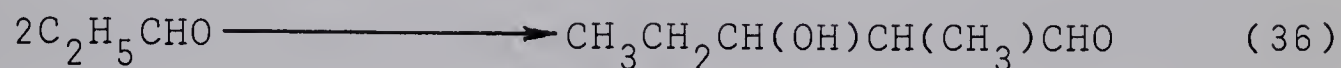
Figure 3

THE PROPOSED REACTION SCHEME

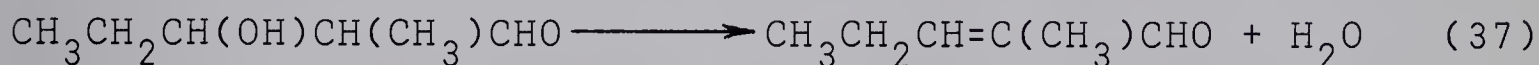


The numbers in parenthesis refer to the reactions explained in the text.

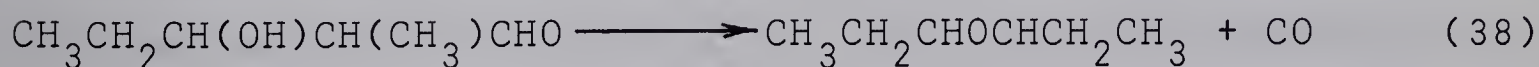
propionaldehyde formed in reaction (34) further condenses to give propionaldol



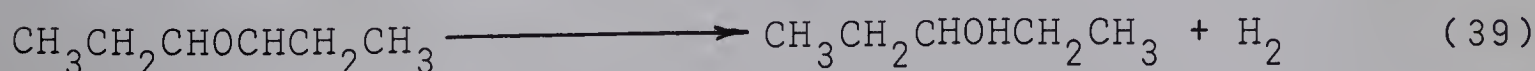
While propionaldol has not been identified in the products of reaction, the aldols are known to be quite unstable and to easily dehydrate to give the corresponding unsaturated aldehyde



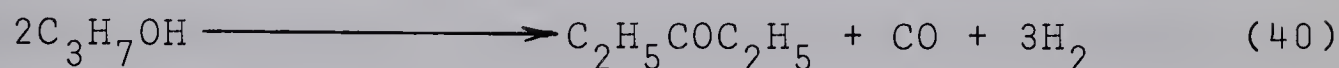
The unsaturated aldehyde, 2-methyl-2-pentenal has been identified in the reaction products and confirms that propionaldol must have been formed. The presence of 3-pentanol in the reaction products may be explained by the decomposition of propionaldol



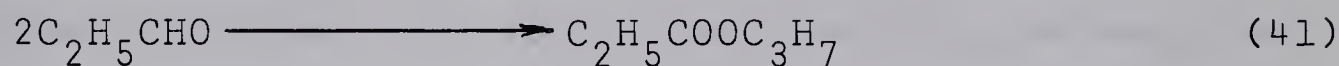
Carbon monoxide has also been identified in the reaction products. The 3-pentanol is then dehydrogenated to give diethyl ketone; the latter has been identified although this may not be the sole origin of the diethyl ketone.



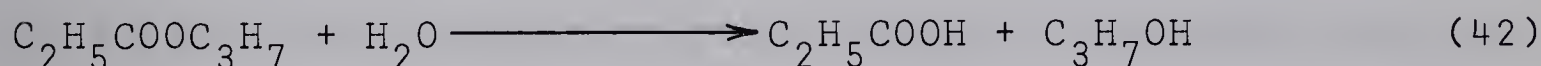
The reactions (34), (36), (38) and (39) represent the aldol route to diethyl ketone, the overall reaction being



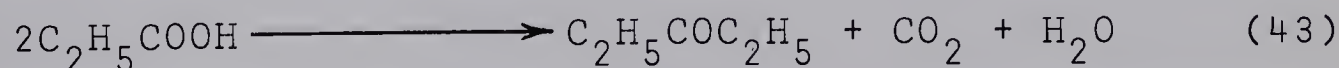
The n-propyl propionate has been identified in the reaction products and may be formed by the alternative condensation of propionaldehyde



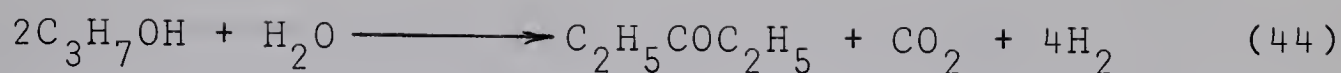
It is suggested that the diethyl ketone may also be formed by the ester route. If water is available, the ester may be hydrolysed to give n-propanol and propionic acid



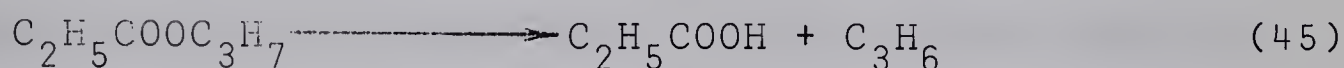
The water required for the hydrolysis of the ester may originate in the reactions (35) and (37). The propionic acid may then decompose to give diethyl ketone



The overall equation for the ester hydrolysis route, reactions (34), (41), (42) and (43), is given by



In addition to the formation of propionic acid from the ester by hydrolysis, n-propyl propionate may directly decompose (without any participation of water) to give propionic acid by the reaction



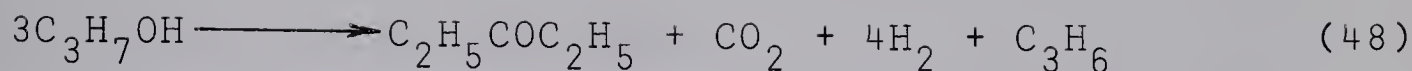
The propionic acid may then decompose according to reaction (43) to form the diethyl ketone. The overall equation, the sum of reactions (34), (41), (45) and (43) is given by



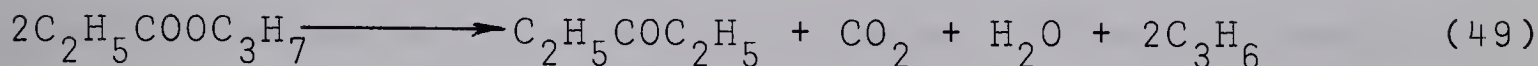
An alternative decomposition of n-propyl propionate, without any participation of water and without any formation of the intermediate propionic acid may take place according to the equation



The overall equation for the direct ester decomposition route, reactions (34), (41) and (47) is given by



Another route, for the direct decomposition of n-propyl propionate, is represented by the equation



The overall equation in this case, the sum of the reactions (34), (41) and (49) is given by the equation (46).

To summarize, there are four possible routes for the formation of diethyl ketone from n-propanol via the ester route

- (a) The ester hydrolysis route, reaction (44).
- (b) The ester decomposition route involving the intermediate propionic acid, reaction (46).
- (c) The ester decomposition route involving the regeneration of n-propanol, reaction (48).
- (d) The direct ester decomposition route, reactions (34), (41) and (49), the overall reaction being the same as for (b).

Routes (b) and (d) represented by the overall equation (46) involve the net formation of water. The possibility of their occurrence under the reaction conditions is ruled out on the basis of the fact that water was not present in the reaction products when the catalysts active for the forma-

tion of diethyl ketone were used.

The propionic acid was not identified in the reaction products. However, its absence from the reaction products does not rule out the possibility of the ester hydrolysis route. It is likely that the acid decomposes to give the ketone as soon as it is formed. The high reactivity of propionic acid, under the reaction conditions used with n-propanol feed, and its ability to produce diethyl ketone was confirmed by carrying out an experimental run with pure propionic acid as the feed. The liquid product was chromatographed and was found to contain diethyl ketone but no propionic acid. However, a quantitative analysis of the product could not be carried out because of the presence of water.

Of the identified compounds all except methyl ethyl ketone, ethyl isopropyl ketone and 3-octanone are accounted for by the proposed reaction scheme shown in Figure 3. The product distribution obtained with diethyl ketone as the feed is reported in Table XVII. The two major products formed were methyl ethyl ketone and ethyl isopropyl ketone and the overall reaction may be written as



Equation (50) suggests that the two ketones formed should be

Table XVII
PRODUCT DISTRIBUTION WITH DIFFERENT FEEDS
Moles per Mole of the Feed

Run No.	19	20	17	21	22
Liquid Feed	PrH	PrH	PrOH	Ester	DEK
Liquid					
Propionaldehyde	0.7310	0.0099	0.0101	0.0256	0.0078
Methyl Ethyl Ketone	Tr	0.0162	0.0200	0.0316	0.0482
n-Propanol	0.0081	Tr	0.0077	0.0142	-
Diethyl Ketone	0.0351	0.2150	0.2360	0.5270	0.7890
Ethyl Isopropyl Ketone	Tr	0.0106	0.0200	0.0261	0.0221
3-Pentanol	Tr	0.0029	0.0046	0.0061	0.0041
n-Propyl Propionate	Tr	Tr	0.0013	0.0033	-
2-Methyl-2-Pentenal	0.0416	Tr	Tr	Tr	-
3-Octanone	Tr	0.0150	0.0192	0.0161	-
Gas					
Hydrogen	0.0904	0.476	1.470	0.978	0.0850
Carbon Monoxide	0.0110	0.116	0.245	0.452	0.0096
Carbon Dioxide	0.0564	0.256	0.231	0.186	0.0708
Propylene	0.0029	0.014	0.047	0.127	0.0032

PrH = Propionaldehyde
PrOH = n-Propanol
Ester = n-Propyl Propionate
DEK = Diethyl Ketone

present in the liquid product in equal molar amounts. Since this was not the case, their different reactivities could conceivably explain the difference in their amounts in the product.

It has not been possible to suggest any reaction to explain the formation of 3-octanone. However, it is not likely that the formation of 3-octanone, an eight carbon compound, is involved in the reaction scheme for the formation of diethyl ketone.

Further information on the chemistry of the reactions catalysed was sought by using the intermediates, propionaldehyde and n-propyl propionate as the reaction feeds.

The product distribution obtained with propionaldehyde as the feed, runs 19 and 20, is reproduced along with that obtained with n-propanol as the feed, run 17, in Table XVII. A comparison of the three runs shows that the same compounds, including n-propanol, are present in the three liquid products. The presence of n-propanol in the liquid product when propionaldehyde is the feed is consistent with the ester routes (a) and (c) proposed above.

The presence of n-propyl propionate in the reaction products and the formation of n-propanol when propionaldehyde is used as the feed suggests that diethyl ketone is formed by the ester route. Conclusive evidence to prove this view was obtained by using pure n-propyl propionate as the feed.

The product distribution obtained with n-propyl propionate as the feed, run 21, is reported in Table XVII and is similar to those obtained with n-propanol and propionaldehyde as the feeds. The fact that the ester decomposes without any participation of water and that diethyl ketone and n-propanol are formed can be explained by reaction (47). Once n-propanol is formed within the catalyst bed it can undergo the reactions suggested earlier to give a product distribution similar to that obtained with n-propanol as the feed.

The evidence presented above leads to the conclusion that the diethyl ketone is formed from n-propanol by three different routes namely, the aldol route, the ester hydrolysis route and the ester decomposition route involving the regeneration of n-propanol.

B. Catalytic Activity

1. Activity of Unsupported Chromia Catalysts

The experimental results obtained with the unsupported chromia catalyst i.e., the sodium hydroxide precipitated chromia catalyst and the ammonium hydroxide precipitated chromia catalyst gel are reported in Table XVIII. The results reported earlier by Komarewsky (28), Hansen (19) and Vasudeva (50) are also included in the same Table for comparison.

The diethyl ketone yield obtained with the sodium hydroxide precipitated chromia catalyst is considerably higher

Table XVIII

ACTIVITY OF UNSUPPORTED CATALYSTS

Run No.	Investigator	Catalyst	Temp. °C	Space Velocity hr ⁻¹	n-Propanol Conversion %	Diethyl Ketone Yield %
-	Komarewsky et al (28)	Sodium Hydroxide Precipitated Chromia	425	0.034*	94.8	48.8
-	Hansen (19)	Chromia on Alumina	475	0.20	68.8	8.7
-	Vasudeva (50)	Chromia on Alumina	455	0.27	96.8	15.2
1	This Work	Sodium Hydroxide Precipitated Chromia	405	0.62	20.0	12.8
2	This Work	Sodium Hydroxide Precipitated Chromia	479	0.57	83.5	37.6
3	This Work	Ammonium Hydroxide Precipitated Chromia Gel	403	0.39	90.8	5.0

* Estimated

than the earlier values of both Hansen and Vasudeva but lower than that reported by Komarewsky and Coley. A diethyl ketone yield of 37.6% at an n-propanol conversion of 83.5% was obtained as compared to the 48.8% diethyl ketone yield at an n-propanol conversion of 94.8% reported by Komarewsky and Coley. The difference can be attributed to the higher space velocity used in the present work. In view of the encouraging diethyl ketone yield obtained it is concluded that the sodium hydroxide precipitated chromia catalyst is quite active for producing diethyl ketone from n-propanol.

With the ammonium hydroxide precipitated chromia gel catalyst the n-propanol conversion was 90.8% while the diethyl ketone yield was only 5.0%.

Komarewsky et al (28) report that their ammonium hydroxide precipitated chromia catalyst was inactive as compared to their sodium hydroxide precipitated catalysts, the ketone yield being only 3.6%. They suggested that the presence of sodium, inevitably retained even after washing the precipitate, in the catalyst has a definite effect on the catalytic activity for the formation of the ketone. By using chromia catalysts with varying sodium content they found (12) that the conversion of n-butyraldehyde to di-n-propyl ketone passed through a maximum. They did not report the nature of side reactions, if any, while using the ammonium hydroxide precipitated chromia catalyst.

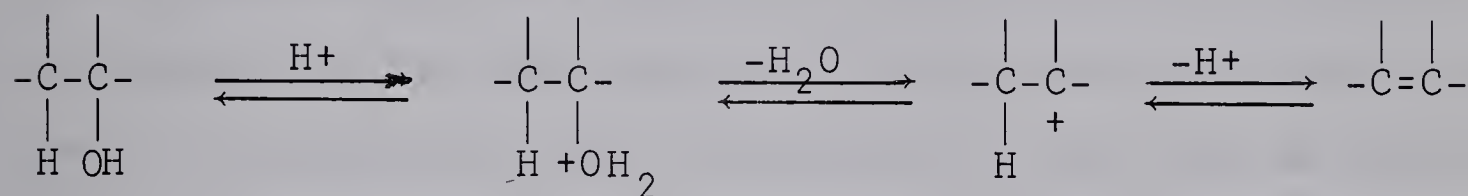
The results obtained with ammonium hydroxide precipitated chromia gel in this study show that a very large proportion of the reacted n-propanol undergoes dehydration to propylene and water. An examination of the reactions discussed earlier, (34) to (49) shows that propylene is formed by the reactions (45), (47) and (49) and water is formed by the reactions (37), (43) and (49) in addition to the dehydration reaction (35). Therefore, it is not possible to assign a quantitative measure of the dehydration of n-propanol when diethyl ketone is also formed. Both the unsupported catalysts result in the formation of diethyl ketone from n-propanol. However, the sodium hydroxide precipitated chromia catalyst does not result in any dehydration to propylene and water except insofar as may be involved in the ester hydrolysis route while the ammonium hydroxide precipitated chromia gel results in appreciable dehydration of n-propanol. An explanation for the difference in the activity of the two chromia preparations may now be sought.

An x-ray diffraction analysis of the two preparations was carried out but both were found to be amorphous. Hence no conclusion could be drawn about any difference in their structure.

The two catalysts were prepared by different methods and may have different physical characteristics. While the possible influence of physical characteristics on the

difference in their catalytic activity cannot be ruled out a logical explanation arises from a consideration of the nature of the dehydration reaction.

The dehydration of alcohols in the liquid phase is believed to take place by carbonium ion mechanism involving an acid catalyst (36).



It is possible that the mechanism with heterogenous catalysts also involves the formation of the carbonium ion. It is, therefore, reasonable to suggest that the chromia catalysts, at least some preparations, possess two (or more) types of sites - acid sites and dehydrogenation sites. When sodium hydroxide is used for preparing the catalyst, the acid sites can be 'neutralised' by sodium hydroxide thereby suppressing the dehydration activity. On the other hand when the precipitation is carried out with ammonium hydroxide, either the neutralisation does not take place or the surface possesses both acidic and basic sites that can catalyse the dehydration of the alcohol by the concerted mechanism. This type of influence of sodium hydroxide and ammonium hydroxide has been observed by Pines et al (39, 40) in the case of alumina catalysts.

It is concluded that the sodium hydroxide precipitated chromia catalyst has appreciable activity for the formation of diethyl ketone from n-propanol and does not result in any dehydration of n-propanol. On the other hand, the ammonium hydroxide precipitated chromia catalyst while active for the formation of diethyl ketone, perhaps predominantly, results in the dehydration of n-propanol. The dehydration activity of chromia may be associated with acid sites which are neutralised if the precipitation is carried out with sodium hydroxide.

2. Activity of Catalyst Supports

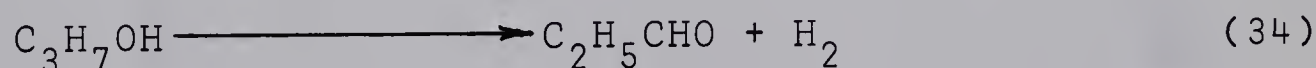
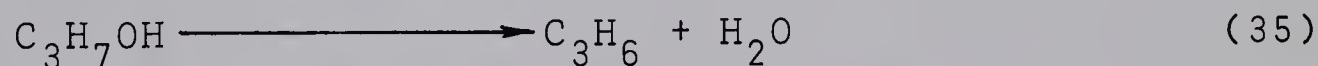
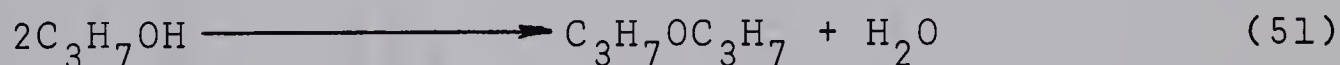
The sodium hydroxide precipitated catalyst, though quite active, was found to lack in physical stability; the catalyst particles disintegrated to a fine powder under the reaction conditions. It was, therefore, considered desirable to investigate the possibility of preparing an active catalyst with adequate physical stability by supporting chromia on a suitable support.

A suitable support must possess the property that is being sought e.g., thermal conductivity, surface area, mechanical strength, etc. In addition, when used for supporting the active component the yield of the required product with the supported catalyst should not be appreciably lower than that obtained with the unsupported catalyst. While the catalytic activities of the support and the active component may not be additive properties it is desirable to check if the support

by itself catalyses any side reactions that may lower the yield of the desired product. The first step then consists essentially in testing the catalytic activity of the arbitrarily chosen porous catalyst supports that possess the required physical property; for the present study the property sought was physical stability under the reaction conditions.

The catalytic activity of three catalyst supports is reported in Table XIX. The interpretation of the results will now be described.

The initial reactions for n-propanol decomposition are dehydration or dehydrogenation, i.e.



The formation of the ether does not take place at high temperatures used in these reactions and both of the remaining reactions produce 1 mole of non-condensable gas per mole of n-propanol reacted. While further decomposition of propionaldehyde and propylene is possible it is clear that every mole of such gas produced represents a maximum of 1 mole of n-propanol decomposed. Since the gas product formed was very

Table XIX

ACTIVITY OF CATALYST SUPPORTS

Run No.	Catalyst	Temp. °C	Space Velocity hr ⁻¹	Gas Evolved Moles/Mole of n-Propanol Feed	Type of Reaction
4	Empty reactor	427	a	9.8×10^{-3}	-
5	Polysurface Alumina	438	0.24	2.46×10^{-2}	Aldehydic Decomposition
6	Pumice	455	0.51	3.5×10^{-2}	Aldehydic Decomposition
7	Norton's Alumina	355	0.58	0.866	Complete Dehydration to Propylene

a Liquid feed rate = 11.7 gms/hr

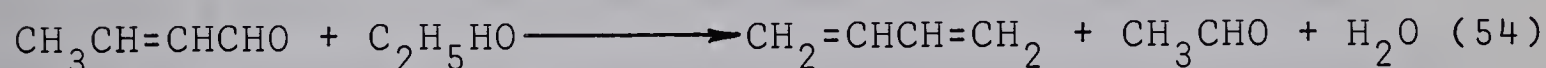
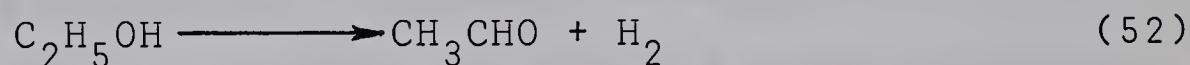
small it was considered adequate to compare the activity of the supports on the basis of the moles of gas produced per mole of the n-propanol feed. The gas produced when polysurface alumina and pumice were used as the catalyst charges being only 2.46×10^{-2} and 3.5×10^{-2} moles per mole of feed it was concluded that these two materials are relatively inactive. While the gas produced was not analysed, an examination of the liquid product by gas chromatography showed them both to contain trace amounts of propionaldehyde. It is therefore concluded that the insignificant decomposition of n-propanol in case of polysurface alumina and pumice is of the aldehydic type and that these two materials are of interest as supports for chromia.

The experimental run carried out to investigate the homogeneous reaction if any and the catalytic activity of the glass wall is also reported in Table XIX. The small amount of gas produced under the reaction conditions shows that the homogeneous reaction and glass catalysed reaction is insignificant.

The results with the Norton's alumina showed it to be very active dehydration catalyst resulting in a complete conversion of n-propanol to propylene and water. It was concluded that the Norton's alumina is of no interest for supporting chromia for the present study.

The significant difference in the catalytic activity

of the two aluminas tested is typical of the state of art of catalysis. This type of apparent discrepancy is often reported in the literature. Thus alumina is generally regarded as a good catalyst for the dehydration of alcohols. On the other hand the production of butadiene from ethanol (15) by the Russian process involves the use of a mixture of alumina and zinc oxide as a catalyst. The reaction is carried out at 400°C and 0.25 atmosphere pressure. The catalyst is supposed to bring about simultaneous dehydrogenation and dehydration. The reactions involved are



The butadiene yield is reported to be 50%. While the details are not available, alumina is reported to catalyse the dehydration of acetaldo1, reaction (53), though any dehydration of ethanol is not mentioned.

Tamele (46) reported that alumina has a very low activity for the cracking reactions while Tung (48) reported alumina to be a good cracking catalyst. In addition, Tung mentions that alumina has dehydrogenation sites.

Thus it is likely that the surface of alumina is quite complex and is capable of catalysing different types of reactions. However, under the conditions of preparation and pretreatment, if any, the activity for a particular type of reaction may be suppressed. If it is assumed that the presence of impurities in polysurface alumina and Norton's alumina does not have any influence on their catalytic activities, it should be possible to modify the activity of Norton's alumina i.e., its dehydration activity can be suppressed.

3. Activity of Pretreated Norton's Alumina

Before attempting to suppress the dehydration activity of Norton's alumina a possible explanation for the difference in the activities of Norton's alumina and polysurface alumina was sought in any difference in their crystal structures. An x-ray powder diffraction pattern for the polysurface alumina was found to be identical with that of α -alumina in spite of the presence of impurities in the sample. On the other hand, Norton's alumina gave a diffraction pattern distinctly different from that of polysurface alumina. The lines were very diffuse and in large number and the interplanar spacings could not be evaluated for identification. The interplanar spacings calculated for polysurface alumina are reported in Appendix III.

Assuming that the catalyst activity was associated with a particular crystalline modification it was argued

that if Norton's alumina could be transformed to the same crystalline structure as the polysurface alumina, its catalytic activity may be modified. Since heating alumina to about 1200°C has been shown by Stumpf et al (45) to transform most aluminas to the α -modification, a sample of the Norton's alumina was heated to 1200°C in air for 1 hour. The x-ray powder diffraction pattern of the heated sample reported in Appendix III matched that of polysurface alumina.

The experimental results for the catalytic activity of the Norton's alumina heated to 1200°C are reported in Table XX along with those for the Norton's alumina. While the catalytic activity of Norton's alumina decreased by heating (compare the temperature required for nearly 100% conversion of n-propanol), the catalyst was still predominantly dehydrating, though some dehydrogenation took place (compare the gas analysis for runs 7 and 8, Table VI) resulting in the formation of a non-aqueous phase containing propionaldehyde, diethyl ketone etc., along with an aqueous phase.

It is therefore concluded that the dehydration activity of alumina is not completely determined by its crystal structure.

Another attempt to suppress the dehydration activity of alumina was based on the generally accepted concept that the catalysts possessing acid sites, and hence capable of dehydrating alcohols, can be poisoned by treatment with an alkaline solution such as that of sodium hydroxide. The

Table XX

ACTIVITY OF PRETREATED NORTON'S ALUMINA

Run No.	Catalyst	Temp.	Space Velocity	% n-Propanol Conversion	Gas evolved moles/mole of feed	Nature of Reaction
7	Norton's Alumina	355	0.58	100.0	0.896	Dehydration to propylene and water
8	Norton's Alumina heated to 1200°C	467	0.39	100.0	0.916	Dehydration and formation of diethyl ketone
9	Base-exchanged Norton's Alumina	352	0.56	Not known	0.036	Not known
10	Base-exchanged Norton's Alumina	461	0.40	95.8	1.64	Formation of diethyl ketone

Norton's alumina was treated with a 2N sodium hydroxide solution. The experimental results showing its catalytic activity are reported in Table XX. A comparison of the gas yield, moles per mole of the n-propanol feed for runs 7 and 9, carried out under similar operating conditions, shows that the activity of the Norton's alumina is considerably decreased by treatment with the sodium hydroxide solution. However, at higher temperature, run 10, the base-exchanged alumina becomes very active and results in the formation of some diethyl ketone. The product distribution for run 10 has already been reported in Table IX.

Normally, n-propanol can undergo dehydration to give di-n-propyl ether, propylene and water. At higher temperatures di-n-propyl ether is not formed so that propylene and water are the only products of dehydration. However, under the reaction conditions of run 10, diethyl ketone is formed involving the reactions (34) to (49) described earlier. As such propylene is formed by the reactions (45), (47) and (49) and water is formed by the reactions (37), (43) and (49) in addition to the dehydration reaction (35). Therefore, it is not possible to assign a quantitative measure of the dehydration of n-propanol when diethyl ketone is also formed. However, in view of the absence of water and rather small amount of propylene present in the liquid product it is believed that the treatment of Norton's alumina with the sodium hydroxide

solution suppressed the dehydration of n-propanol.

It was expected that the treatment of the Norton's alumina with the sodium hydroxide solution would suppress its dehydration activity but the parallel development of the activity for forming diethyl ketone was not expected. A comparison of this result with those reported in the literature will now be made.

The experimental work reported in the literature on the reactions of alcohol in the presence of alumina catalysts can be broadly classified by two approaches:

1. Pines and co-workers (39, 40) studied the nature of alumina surface by investigating its activity for different types of reactions. They found that alumina results in the dehydration of 1-butanol and that its dehydrating activity is due to the acid centres. A treatment of alumina with ammonia results in a preferential poisoning of the 'strong acid sites'; the carbonium ion character of dehydration is suppressed and the alumina has, after treatment, both acidic and basic sites and the dehydration takes place by a concerted mechanism. The treatment of alumina with a sodium hydroxide solution almost completely poisons its dehydrating activity for 1-butanol. Since no other reaction was reported it is implied that the poisoned catalyst became inactive towards 1-butanol.

2. The second approach consists in studying a single reaction with a series of catalysts. Mars et al (34) have reviewed the decomposition of formic acid in the presence of oxide catalysts. Both formic acid and ethanol decompose in the presence of the oxides of magnesium, zinc, iron, chromium, titanium, silicon and aluminum used individually as the catalysts to give dehydration and dehydrogenation products. If selectivity is defined as the ratio of the dehydrogenation to the total decomposition, it has been found that the selectivity for the decomposition of both formic acid and ethanol increases with increase in the basicity of the catalyst. Thus the dehydration activity increases and the dehydrogenation activity decreases in the order in which the catalysts are reported, i.e., the magnesium oxide is predominantly dehydrogenating and the alumina is predominantly dehydrating. In the case of the formic acid decomposition it has been reported that 'the presence of foreign metallic ions can enhance the dehydrogenation activity. The addition of 5 to 30% K_2CO_3 to silica promotes dehydrogenation; lithium and magnesium ions also act as promoters. Also on ZnO the addition of alkali (Li or Na) increases the rate of dehydrogenation.' The parallelism observed between the activity

and the selectivity of the oxide catalysts for the decomposition reactions of both formic acid and ethanol (both undergo dehydration and dehydrogenation) suggests that the influence of the alkalis observed in the case of formic acid would perhaps apply to the reactions of ethanol (and hence the other alcohols). While the detailed results on the influence of the alkalies on the reactions of formic acid are not available, it appears that the presence of the alkalies increases the rate of dehydrogenation without appreciably influencing the rate of dehydration.

Thus, these two viewpoints suggest that the treatment of alumina with the sodium hydroxide solution would either completely suppress the dehydration activity, without any other reaction taking place or would increase the rate of dehydrogenation without influencing the rate of dehydration. On the other hand the results obtained in the present investigation show that by the treatment of alumina with the sodium hydroxide solution not only dehydration is suppressed and the dehydrogenation of n-propanol becomes significant, the n-propanol is converted to diethyl ketone by the reaction scheme shown in Figure 3. To the best of the author's knowledge, the ability of alumina to catalyse the formation of diethyl ketone from n-propanol has been observed for the first time. While the presence of the impurities in the catalyst must be recognized,

it may be tentatively suggested that the impurities are of little significance from the point of view of catalytic activity and that the type of activity described herein may be associated with alumina and its modifications. It must be pointed out that Ipatieff's results (26) for the formation of acetone from ethanol using alumina catalyst showed considerable dehydration of ethanol and the information on the catalyst was not given.

4. Activity of Supported Chromia

The experimental results obtained with chromia on pumice catalyst are shown in Table XXI. Although the n-propanol conversion was 43.3%, diethyl ketone was not formed. The liquid product consisted essentially of propionaldehyde and unreacted n-propanol, though some unidentified products were present in the liquid product. The product distribution, Table XXI, shows that 0.128 moles of propylene were formed per mole of the n-propanol feed. Since water did not appear in the products, it is unlikely that the propylene was formed by the direct dehydration of n-propanol. Of the 34.3% n-propanol reacted, only 19.9% was represented by propionaldehyde in the product the rest being lost through unknown reaction.

The possibility of any promotion of chromia by sodium, as suggested by Coley (12) was evaluated by testing the activity of the sodium hydroxide treated chromia on pumice catalyst and the results are reported in Table XXI. The

Table XXI

ACTIVITY OF SUPPORTED CHROMIA CATALYSTS

Run No.	Catalyst	Temp. °C	Space Velocity hr-1	n-Propanol Conversion %	Diethyl Ketone Yield %	Moles of Product per Mole of n-Propanol Feed Propionaldehyde Propylene
11	Chromia on pumice	451	0.49	34.3	0.0	0.1280
12	NaOH treated Chromia on pumice	455	0.53	18.0	0.0	0.1080
13	Chromia on Polysurface alumina	450	0.32	33.9	0.0	0.0914
14	Chromia on Polysurface alumina	478	0.33	50.8	0.0	0.1262
17	Base-exchanged Chromia on Norton's alumina	467	0.37	99.2	47.6	0.0470

n-propanol conversion was only 18.0% as compared to the 34.3% n-propanol conversion obtained with the chromia on pumice catalyst under similar reaction conditions. The liquid product consisted primarily of propionaldehyde and the unreacted n-propanol. No water was found in the products of reaction. Even though the propionaldehyde formed per mole of the n-propanol feed decreased appreciably, the propylene formed remained the same. In view of the results presented earlier it is to be expected that if propylene were formed by the direct dehydration of n-propanol, a treatment of the catalyst with a sodium hydroxide solution would suppress its formation. Since propylene was formed in comparable amounts even after the sodium hydroxide treatment of the chromia on pumice catalyst, it supports the view that propylene was not formed by the direct dehydration of n-propanol. Diethyl ketone was not formed even though the propionaldehyde was formed. This implies that the sodium does not catalyse the formation of diethyl ketone from n-propanol.

The experimental results obtained with the chromia on polysurface alumina catalyst are reported in Table XXI. Even at an n-propanol conversion level of 47.8% diethyl ketone was not formed. The liquid product consisted primarily of propionaldehyde, n-propanol and a small amount of n-propyl propionate. The gas product contained appreciable amount of propylene; since water was not found in the liquid

product it is unlikely that the propylene was formed by the direct dehydration of n-propanol.

While an unsupported chromia catalyst is quite active for forming diethyl ketone from n-propanol, the supported chromia catalysts described above are quite inactive despite the fact that the supports are inactive by themselves.

The base-exchanged Norton's alumina was found to be active for the formation of diethyl ketone from n-propanol; the diethyl ketone yield being 42.2%. The possibility of obtaining a higher diethyl ketone yield by a catalyst that combines chromia and the base-exchanged Norton's alumina was investigated. The impregnation of base-exchanged Norton's alumina with chromia from a chromium nitrate solution was not considered useful as the chromium nitrate solution is acidic and may reactivate the acidic properties of the alumina. Instead the Norton's alumina was impregnated with chromia (from chromium nitrate solution followed by drying and decomposing the nitrate) and reduced to convert the water soluble CrO_3 to the water insoluble Cr_2O_3 . The supported catalyst was then base-exchanged with the sodium hydroxide solution. The catalytic activity of the base-exchanged chromia on Norton's alumina is also reported in Table XXI. The diethyl ketone yield was found to be 47.2%.

C. A Test for the Proposed Reaction Scheme

The three catalysts found to be active for the forma-

tion of diethyl ketone from n-propanol are

1. Sodium hydroxide precipitated chromia.
2. Base-exchanged Norton's alumina.
3. Base-exchanged chromia on Norton's alumina.

A comparison of the product distributions obtained with these catalysts, reported in Table XXII, shows that the same identified products were formed in similar proportions for each of the three catalysts suggesting that the formation of the diethyl ketone follows the same reaction sequence in each case.

On the basis of the identified products and the tests with intermediates, propionaldehyde and n-propyl propionate, it was shown that the formation of the diethyl ketone takes place by the aldol route and the ester decomposition route involving the regeneration of n-propanol. It was further suggested that the diethyl ketone may also be formed by the ester hydrolysis route. To recapitulate the overall equations may be rewritten;

for the aldol route



for the ester decomposition route involving the regeneration of n-propanol

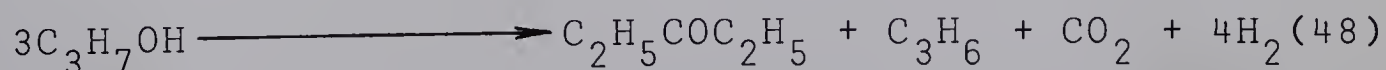


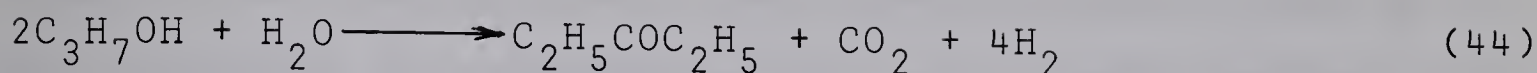
Table XXII

PRODUCT DISTRIBUTION

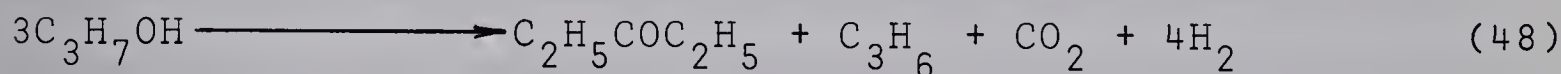
Moles per Mole of n-Propanol Feed

Catalyst	NaOH ppted Chromia	Base-exchanged Norton's Alumina	Base-exchanged Chromia on Norton's Alumina
Run No.	2	10	16
Liquid			
Propionaldehyde	0.1500	0.0118	0.0972
Methyl Ethyl Ketone	0.0229	0.0180	0.0092
n-Propanol	0.1650	0.0415	0.1510
Diethyl Ketone	0.1570	0.2020	0.1430
Ethyl Isopropyl Ketone	0.0044	0.0169	0.0112
3-Pentanol	0.0027	0.0065	0.0041
n-Propyl Propionate	0.0083	Tr	0.0027
2-Methyl-2-Pentenal	0.0044	Tr	0.0142
3-Octanone	0.0066	0.0164	0.0191
Gas			
Hydrogen	1.160	1.210	1.120
Carbon Monoxide	0.140	0.189	0.123
Carbon Dioxide	0.135	0.197	0.147
Propylene	0.036	0.047	0.025

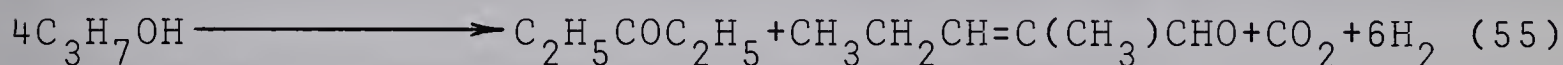
for the ester hydrolysis route



If dry n-propanol is used as the feed, the water required for the hydrolysis of the ester, reaction (42), may originate in the dehydration of n-propanol, reaction (35), or the dehydration of propionaldol, reaction (37), in which case the overall equations are



and



An examination of the overall equations (40), (48) and (55) shows that for every mole of the diethyl ketone formed, the moles of n-propanol reacted are two, three or four depending on the reaction route. The diethyl ketone yield reported in this study has been defined as

% Diethyl ketone yield

$$= \frac{2 \times \text{moles of diethyl ketone in the product/mole of n-propanol in the feed}}{\% \text{ n-propanol conversion}}$$

If two moles of n-propanol react to give one mole of diethyl ketone as by the aldol route, reaction (40), the above definition

is appropriate as it gives a 100% diethyl ketone yield if all the n-propanol is converted to give only diethyl ketone. However, three or four moles of n-propanol are required to form one mole of diethyl ketone if the other routes are involved. The inadequacy of the above definition, or any other definition based on any single overall equation, is quite apparent. In order to get a true measure of the diethyl ketone yield that would give a value of 100% if all the n-propanol reacted to give only diethyl ketone by all the routes, quantitative information on the relative importance of the various routes is required. An attempt to deduce this information from the product distributions for the various runs and the stoichiometry of the overall reactions will now be explained.

An examination of the overall reactions (40), (48) and (55) shows that carbon dioxide is formed by the ester routes and carbon monoxide by the aldol route. In the case of the ester route the diethyl ketone is formed in the same reaction step as the carbon dioxide and their molar ratio is one. In the case of the aldol route, carbon monoxide is formed by reaction (38), while diethyl ketone is formed by reaction (39). If it is assumed that carbon monoxide and carbon dioxide are not formed by any other reactions and that the 3-pentanol reacts only by reaction (39), the amount of diethyl ketone formed by the ester routes and the aldol route can be calculated. Furthermore, if it is assumed that the water formed by the

dehydration of propionaldol, reaction (37) is consumed for the hydrolysis of the ester, reaction (42), and that the 2-methyl-2-pentenal does not react any further, the amount of n-propanol reacted by the three routes and the hydrogen formed can be calculated. To these values of the reacted n-propanol and the hydrogen formed the values corresponding to propionaldehyde, 3-pentenal, n-propyl propionate and 2-methyl-2-pentenal can be added to give the calculated values of n-propanol reacted and the hydrogen formed. Also the diethyl ketone formed by the overall reaction (48) can be separated from that formed by the overall reaction (55). A quantitative check for the calculated values of the n-propanol reacted and the diethyl ketone and the hydrogen formed with the corresponding experimental values would then lend further evidence to the proposed reaction scheme and also establish a quantitative evaluation of the relative importance of the ester routes and the aldol route.

The calculated values for the n-propanol accounted, the diethyl ketone and the hydrogen formed per mole of n-propanol in the feed are given in Table XXIII. The diethyl ketone formed by the aldol route and the ester routes has also been reported separately. The experimental values for the diethyl ketone and the hydrogen formed are also included in the Table. The sample calculations for run 16 are shown in Appendix IV.

Table XXIII

TEST FOR THE PROPOSED REACTION SCHEME

Basis: 1 Mole of n-Propanol Feed

Run No.	1	2	10	15	16	17	18
DEK via the aldol route *	0.005	0.137	0.183	0.015	0.119	0.240	0.209
DEK via the ester routes *	0.022	0.135	0.197	0.035	0.147	0.231	0.213
Total Calculated DEK	0.027	0.272	0.380	0.050	0.266	0.471	0.422
Experimental DEK	0.013	0.157	0.202	0.015	0.143	0.236	0.244
Calculated n-PrOH	0.968	1.034	1.035	0.972	0.983	1.213	1.083
Calculated H ₂	0.225	1.170	1.380	0.406	1.113	1.680	1.509
Experimental H ₂	0.244	1.160	1.210	0.391	1.120	1.470	1.500
Carbon Balance	92.7	84.6	67.8	90.1	72.8	74.5	74.5
% Liquid Product Retained by Chromat. Column	6.5	19.0	36.7	9.0	28.5	26.2	30.2

* Calculated

1. Interpretation of the Calculated Results

A close check between the calculated and the experimental values for the n-propanol reacted and the hydrogen formed is observed. However, the diethyl ketone formed is quite low as compared to the calculated amount. This suggests that some of the diethyl ketone formed decomposes further. The results of an experimental run with diethyl ketone as the feed, reported in Table XVII, show that some of the diethyl ketone decomposes further and that some carbon monoxide and carbon dioxide are formed by reactions other than those included in the overall reactions (40), (48) and (55). Thus the discrepancy between the calculated diethyl ketone and the actual diethyl ketone can be explained partly by the further decomposition of the diethyl ketone formed and partly by the carbon monoxide and the carbon dioxide formed by reactions other than those included in the overall reactions (40), (48) and (55).

Since carbon monoxide and carbon dioxide are also produced by reactions other than those involved in the overall reactions (40), (48) and (55), the values of the calculated n-propanol should be correspondingly higher than 1.0 or if the amounts of carbon monoxide and carbon dioxide formed by only reactions (40), (48) and (55) were available the calculated n-propanol values would be lower than those reported in the Table XXIII. The difference then corresponds to the amount of n-propanol that must have undergone reactions other

than those included in the reaction scheme described earlier. Since the proposed reaction scheme takes into account the major components separated by the chromatographic technique used, some other compounds must be formed. A carbon balance for the different runs shows that nearly 7 to 32% of the carbon in the feed is not accounted for in the identified reaction products. An analysis of the liquid product by vapor phase chromatography also showed that nearly 3 to 36% of the liquid product was retained by the chromatographic column in the various runs. It is likely that the compounds retained by the chromatographic column are high molecular weight compounds, formed probably by the further condensation of propionaldehyde, propionaldol and 2-methyl-2-pentenal, that represent both the carbon not accounted for by the identified reaction products and the n-propanol difference between the values calculated by using the total carbon monoxide, carbon dioxide and 2-methyl-2-pentenal formed and those directly involved in the reactions represented by equations (40), (48) and (55). This shows that a close check for the calculated n-propanol, even when carbon balance is low, is merely a coincidence and that some condensation products were formed. A similar argument explains the close check obtained for hydrogen and suggests that the unidentified products possibly result from the condensation of propionaldehyde, propionaldol and 2-methyl-2-pentenal.

An examination of reaction (48) also shows that for every mole of carbon dioxide formed one mole of propylene is formed. The fact that propylene is present in the product in amounts smaller than carbon dioxide cannot be used to argue that the ester route is insignificant and that the carbon dioxide is formed by reactions other than those involved in reaction (48) since propylene is known to react further in the presence of chromia-alumina catalysts (41).

The analysis carried out above does not enable an evaluation of the relative importance of the various routes. Therefore the diethyl ketone yield as defined earlier has been arbitrarily accepted. However, the following general observations may be made:

1. The diethyl ketone formed decomposes further under the reaction conditions.
2. Carbon monoxide and carbon dioxide are also formed by reactions other than those involved directly in the aldol route and the ester routes.
3. A certain amount of n-propanol reacts, through propionaldehyde, to result in condensation products thus lowering the diethyl ketone yield.

If it is recognized that some of the diethyl ketone formed reacts further and that carbon monoxide and carbon dioxide are also formed by reactions other than those involved in the overall reactions (40), (48) and (55), it is clear from

Table XXIII that carbon monoxide or carbon dioxide alone is not enough to account for the diethyl ketone formed. In other words both the aldol and the ester routes must be participating in the formation of diethyl ketone. Komarewsky and Coley while reporting their results on the conversion of normal alcohols, ranging from propyl to octadecyl, to the corresponding ketones state (29) that 'Subsequent analysis of the non-condensable product gas indicate that the gases consisted largely of hydrogen and carbon monoxide present in a ratio of three volumes of hydrogen to one of carbon monoxide' their published gas analysis (available for runs with n-hexyl to n-octyl alcohols only) show that carbon dioxide was also produced in amounts comparable to carbon monoxide (28) indicating that the ester route was possibly playing some role in the formation of the ketones under their reaction conditions.

The diethyl ketone is formed from n-propanol under the reaction conditions by the aldol route as well as the ester routes and the amount of n-propanol required to form one mole of diethyl ketone varies with the reaction route. This suggests that an efficient use of n-propanol requires that the catalyst should catalyse only the aldol route or that if the ester route is catalysed water should be added with the n-propanol feed in the hope that the diethyl ketone yields are improved.

D. A Comparison of the Performance of the Active Catalysts

The ultimate criterion for comparing the performance of different catalysts is the cost per unit of product in an industrial reactor. While such information is beyond the scope of a laboratory investigation such as the one described in the present study it may be pointed out that the highest diethyl ketone yield was obtained with the base-exchanged chromia on Norton's alumina (see Table XXIV). Under the same operating conditions a 5.4% higher diethyl ketone yield was obtained with the base-exchanged chromia on Norton's alumina catalyst as compared to the base-exchanged Norton's alumina catalyst. The unaccounted carbon has been associated in earlier discussion with the condensation products. A 6.7% lower carbon balance with the base-exchanged Norton's alumina catalyst suggests that it catalyses the condensation reactions to a greater extent than the base-exchanged chromia on Norton's alumina does. The highest diethyl ketone yield obtained with the sodium hydroxide precipitated chromia catalyst, under the operating conditions used, was only 37.6%. Both of the base-exchanged catalyst possess the advantage of physical stability with respect to size, under the operating conditions, as compared to the sodium hydroxide precipitated chromia catalyst.

E. Influence of Temperature on the Activity of the Base-Exchanged Chromia on Norton's Alumina

The experimental results showing the influence of

Table XXIV

PERFORMANCE OF THE ACTIVE CATALYSTS

Catalyst	NaOH pptd. Chromia	Base-exchanged Norton's Alumina	Base-exchanged Chromia on Norton's Alumina	
Run No.	2	10	17	18
Temperature, °C	479	467	467	479
Space Velocity, hr ⁻¹	0.57	0.37	0.37	0.38
n-PrOH Conversion %	83.5	95.8	99.2	100.0
DEK yield	37.6	42.2	47.6	48.8
Carbon Balance	84.6	67.8	74.5	74.5

temperature on the diethyl ketone yield obtained with the base-exchanged chromia on Norton's alumina as catalyst are reported in Table XXV. The % carbon unaccounted in the identified products per mole of the reacted n-propanol is reported in the Table and is found to increase with temperature showing that as the temperature is increased the amount of n-propanol reacting to give the condensation products increases. However, the diethyl ketone yield based on the reacted n-propanol still keeps increasing. A part of the increase in the diethyl ketone yield with increasing temperature is due to the increasing amounts of intermediates, particularly propionaldehyde, reacting further to give diethyl ketone as the intermediates are not taken into account while calculating the diethyl ketone yield. Thus if the amount of n-propanol equivalent to the intermediates, propionaldehyde, n-propyl propionate and 3-pentanol, is taken into account as the unreacted n-propanol the redefined diethyl ketone yield, shown as the corrected diethyl ketone yield in Table XXV is higher than the diethyl ketone yield. An increase in the corrected diethyl ketone yield with temperature can, however, only be ascribed to the increasing importance of the aldol route as compared to the ester route. While the quantitative evaluation of the relative importance of the aldol and the ester route could not be carried out, if it is assumed that the carbon monoxide and the carbon dioxide are produced by

Table XXV

INFLUENCE OF TEMPERATURE ON CATALYTIC ACTIVITY

Catalyst: Base-exchanged Chromia on Norton's Alumina

Liquid Feed: n-Propanol

Run No.	15	16	17	18
Temperature, °C	403	446	467	479
Space Velocity, hr ⁻¹	0.38	0.37	0.37	0.38
% Carbon Unaccounted per Mole of the Reacted n-Propanol	8.9	22.1	25.8	26.4
Diethyl Ketone Yield	8.1	33.7	47.6	48.8
Corrected Diethyl Ketone Yield	16.4	40.9	48.6	49.7
CO:CO ₂	0.428	0.836	1.06	1.00

reactions other than those involved in (40), (48) and (55) in proportions similar to their ratio in the total product, then the latter gives a measure of the relative importance of the aldol and the ester routes. The $\text{CO}:\text{CO}_2$ ratio shown in Table XXV shows that with an increase in temperature the importance of the aldol route increases.

VI CONCLUSIONS

1. Two chromia catalysts prepared by precipitation were found to catalyse the decomposition of n-propanol. The sodium hydroxide precipitated chromia catalysed the formation of diethyl ketone from n-propanol; at a temperature of 479°C and a space velocity of 0.57 hr^{-1} the diethyl ketone yield was 37.6%, the n-propanol conversion being 83.5%. On the other hand, the ammonium hydroxide precipitated chromia catalysed mainly the dehydration of n-propanol resulting in the formation of propylene and water although some diethyl ketone was also formed; at a temperature of 403°C and a space velocity of 0.39 hr^{-1} the diethyl ketone yield was only 5.0%, the n-propanol conversion being 90.8%.
2. Pumice and polysurface alumina were found to be nearly inactive for catalysing the reactions of n-propanol. Chromia catalysts prepared by the impregnation of chromia on pumice and polysurface alumina catalysed the decomposition of n-propanol but did not result in the formation of diethyl ketone. Of the 34.3% n-propanol reacted in the presence of chromia on pumice catalyst at 451°C and a space velocity of 0.49 hr^{-1} , 19.9% was

converted to propionaldehyde. Of the 50.8% n-propanol reacted in the presence of chromia on polysurface alumina at 478°C and a space velocity of 0.33 hr^{-1} , 22.6% was converted to propionaldehyde. Treatment of chromia on pumice with sodium hydroxide did not result in any promotion of the catalyst to form diethyl ketone from n-propanol.

3. Norton's alumina was found to catalyse the dehydration of n-propanol to propylene and water; the n-propanol conversion was 100% at a temperature of 355°C and a space velocity of 0.58 hr^{-1} . Heating Norton's alumina to 1200°C in air was found to decrease its dehydrating activity, simultaneously resulting in some dehydrogenation activity. Treatment of Norton's alumina with sodium hydroxide solution completely changes its catalytic activity and diethyl ketone is formed; at a temperature of 461°C and a space velocity of 0.40 hr^{-1} the diethyl ketone yield was 42.2%, the n-propanol conversion being 95.8%.

4. The base-exchanged chromia on Norton's alumina was found to catalyse the formation of diethyl ketone from n-propanol; at 479°C and a space velocity of 0.38 hr^{-1} the diethyl ketone yield was 48.8%, n-propanol conversion being 100.0%.

5. The identified reaction products and the experimental runs with propionaldehyde and n-propyl propionate as feeds lead to the conclusion that the diethyl ketone is formed from n-propanol by three routes simultaneously - the aldol route, the ester decomposition route involving the regeneration of n-propanol and the ester hydrolysis route.

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APPENDIX I

PROPERTIES OF CATALYST SUPPORTS

The physical characteristics and the chemical composition of the catalyst supports, used in the present investigation, as reported in the manufacturer's catalogues, are given below:

1. Polysurface alumina:

Supplied by	: The Carborundum Co.
Manufacturer's designation	: Polysurface pellets AMM
Primary material	: Fused aluminum oxide
Physical characteristics	: Irregular rough surface structure; -2+4 mesh size; porosity, 40-50%; approxi- mate average pore size, 50-100 microns; surface area, less than 1 sq. meter/gm.
Chemical composition	: Al_2O_3 , 83.58; SiO_2 , 11.00; Fe_2O_3 , 1.04; TiO_2 , 2.22; CaO , 1.39; MgO , 0.30; Na_2O , 0.08; K_2O , 0.39.

2. Norton's alumina:

Supplied by	: Norton Co. of Canada, Ltd.
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Manufacturer's designation : Alundum catalyst carrier

LA-617

Physical characteristics : 1/8" x 1/8" cylindrical pellets; porosity, 60-65%; water absorption, 51-56%; surface area, 60-70 sq. meters/gm; x-ray diffraction analysis showed predominantly γ -alumina with some α -alumina and quartz.

Chemical composition : Al_2O_3 , 77.0; SiO_2 , 21.2; Fe_2O_3 , 0.2; TiO_2 , 0.5; Na_2O , 0.5; K_2O , 0.2; MgO , 0.2; CaO , 0.2.

3. Pumice:

Supplied by : Charles A. Wagner Co., Inc., Philadelphia 40.

Physical characteristics : -8+14 mesh irregular shaped particles.

Chemical composition : SiO_2 , 71.8; Al_2O_3 , 13.96; MgO , 0.11; Fe(O) , 1.92; Mn(O) , 0.08; Na_2O and K_2O (combined), 12.13.

APPENDIX II

CATALYST PREPARATION

The experimental procedures used for preparing the catalyst, investigated in the present study are given in the following sections:

Materials:

1. Chromium nitrate, B.D.H. reagent grade, chemical formula $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.
2. Sodium hydroxide pellets, reagent grade, chemical formula NaOH .
3. Ammonium hydroxide, reagent grade, 28-29% ammonia in water.
4. Polysurface alumina supplied by Carborundum Co.
5. Pumice supplied by Charles A. Wagner Co., Inc.
6. Norton's alumina supplied by Norton Co. of Canada Ltd.

Methods of preparation:

1. Sodium hydroxide precipitated chromia catalyst
500 cc of 1N solution of chromium nitrate in distilled water at room temperature were neutralised by rapidly adding 500 cc of 1N sodium hydroxide solution. A very voluminous precipitate was obtained which was filtered, washed with

distilled water and dried at $105 \pm 5^\circ\text{C}$ for 6 hours. The filter cake during drying broke down to friable shining particles ranging in size from about 4 mesh to fine powder. The colour of the apparently dry catalyst was dark blue. The coarser fraction, -4+20 mesh was charged into the reactor and heated to about 450°C for further removal of water. The catalyst was dried till further removal of water stopped and was reduced by passing n-propanol for two hours at a space velocity of 0.63 hr^{-1} , maintaining the catalyst temperature at about 450°C . The final product was bright green in colour with a few dark particles and was ready for use. This method is essentially the same as that used by Komarewsky and Coley (28) for one of their preparations.

2. Ammonium Hydroxide Precipitated Chromia Gel

This catalyst was prepared by the method of Turkevich, Fehrer and Taylor (49).

200 grams of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 66 grams of ammonium acetate were dissolved in 120 cc of distilled water. The solution was heated to boiling for a brief interval of time and cooled to room temperature. A solution of 180 cc of ammonium hydroxide (28-29% NH_3 in water) in 250 cc of distilled water was then added with stirring and the whole warmed on a water bath whereupon a jelly was formed that entrapped all the water in its structure. This jelly was partially dried at $55 \pm 5^\circ\text{C}$ for 12 hours. The partially dried

jelly disintegrated into small dark blue shiny particles which were thoroughly washed with distilled water, filtered and dried at $105 \pm 5^\circ\text{C}$ for 6 hours. The apparently dry catalyst was charged into the reactor and heated to 450°C for further removal of water. The catalyst was then reduced by n-propanol as in the case of the sodium hydroxide precipitated chromia catalyst.

Gel formation is a special case of precipitation in which the precipitation is delayed till all the components have been thoroughly mixed. However, preparation of gels requires a close specification of experimental conditions. During the course of experimental work it was found that in some cases the jelly did not set by following the above procedure. It was found that the pH of the solution after the addition of ammonium hydroxide solution is critical and that the jelly does not set on warming the solution if its pH is less than 7.0. However, if the pH of the solution is 7.0 to 7.2 the jelly sets on warming the solution for about 15 minutes. This required the addition of more ammonium hydroxide, than given above, in some cases.

3. Norton's alumina

The $1/8'' \times 1/8''$ cylinders supplied by Norton Co. of Canada were crushed and screened to give -10+20 mesh fraction.

4. Polysurface alumina

The -2+4 mesh polysurface alumina supplied by Carborundum Co. was crushed and screened to obtain -10+20 mesh fraction.

5. Pumice:

Pumice supplied by Charles A. Wagner Co., Inc., was used as such.

6. Base-exchanged Norton's alumina

A 25 gram sample of Norton's alumina was immersed in 100 cc of 2N sodium hydroxide solution at room temperature for 6 hours. The excess solution was drained off and the wet solids dried at $105 \pm 5^\circ\text{C}$ for 1 hour.

7. Chromia on pumice

25 grams of pumice were immersed in 100 cc of 2N chromium nitrate solution in distilled water at room temperature for 1 hour. The excess solution was drained off and the wet solids dried at $105 \pm 5^\circ\text{C}$ for 1 hour. The dried solids were heated up to 300°C to decompose the nitrate. The resulting oxide was reduced with n-propanol as in the case of the sodium hydroxide precipitated chromia catalyst.

8. Sodium hydroxide treated chromia on pumice

25 grams of the reduced chromia on pumice was immersed in 100 cc of 2N sodium hydroxide solution at room temperature for 6 hours. The excess solution was drained

off and the wet solids dried at $105 \pm 5^\circ\text{C}$ for 1 hour.

9. Chromia on polysurface alumina

50 grams of polysurface alumina were immersed in 100 cc of 2N chromium nitrate solution in distilled water. It was observed that the penetration of the solution into the pores of the support was more difficult than that observed with pumice. This required longer contact between the solid and the solution for proper impregnation. The solids and the solution were left in contact overnight. The excess solution was drained off and the solids dried at $105 \pm 5^\circ\text{C}$ for 1 hour. The dried catalyst was heated to 300°C to decompose the nitrate. The resulting oxide was reduced with n-propanol as in the case of the sodium hydroxide precipitated chromia catalyst.

10. Base-exchanged chromia on Norton's alumina

25 grams of Norton's alumina were immersed in 100 cc of 2N chromium nitrate solution in distilled water for 1 hour. The excess solution was drained off and the wet solids were dried at $105 \pm 5^\circ\text{C}$ for 1 hour. The dried solids were charged into the reactor and heated up to 300°C to decompose the nitrate. The oxide was then reduced by passing n-propanol over it at 450°C and a space velocity of 0.37 hr^{-1} for two hours. The reduced catalyst was cooled in place while passing nitrogen over it. The cooled solids were immersed

in 100 cc of 2N sodium hydroxide solution for 6 hours. The excess solution was drained off and the solids were dried at $105 \pm 5^{\circ}\text{C}$ for 1 hour.

APPENDIX III

X-RAY POWDER DIFFRACTION ANALYSIS

The X-ray powder diffraction analysis of polysurface alumina and Norton's alumina heated to 1200°C were carried out by using a Phillips X-ray diffraction generator Model PW 1009 using a cobalt target and an iron filter. Microdensitometer was used to measure the distances between the rings. The Bragg's angle θ was calculated and the interplanar spacings were evaluated by the relation.

$$d = \frac{\lambda}{2 \sin \theta}$$

The ASTM index card 10-173 (for α -alumina) was used as the references for comparing the calculated interplanar spacings for the samples in question. Of the 49 lines reported in the reference card only 13 have a relative intensity above 10, the intensity of the darkest line being 100. Since the relatively weaker lines on the powder photographs could not be measured accurately by the Microdensitometer, only the stronger lines were used for comparison. The interplanar spacings d in Angstroms for the samples studied are reported along with those from the ASTM index card in the Table below.

INTERPLANAR SPACINGS

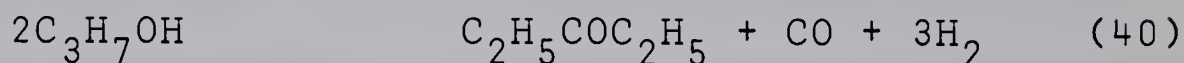
ASTM Index Card		Polysurface Alumina	Norton's Alumina Heated to 1200°C
d,A	I _{relative}	d,A	d,A
3.479	75	3.435	3.428
2.552	90	2.544	2.526
2.379	40	2.380	2.354
2.085	100	2.090	2.079
1.740	45	1.735	1.724
1.6101	80	1.610	1.605
1.404	30	1.406	1.428
1.374	50	1.374	1.365
1.239	15	1.235	1.233
1.043	13	1.042	1.041
0.998	11	0.995	0.995
0.908	13	0.907	0.906

SAMPLE CALCULATIONS FOR THE TEST OF THE
PROPOSED REACTION SCHEME

Basis: 1 Mole of the n-Propanol Feed

The data used for the sample calculations are reported in Table XII as run 16.

The overall equation for the aldol route is



For every mole of diethyl ketone formed by the aldol route one mole of carbon monoxide is formed. However, carbon monoxide is formed by the step involving the decarbonylation of propionaldol. Therefore, the 3-pentanol formed that has not reacted to give the diethyl ketone has to be taken into account for calculating the diethyl ketone formed by the aldol route. Assuming that carbon monoxide is not formed by reactions other than those involved in (40) and does not react further and that the 3-pentanol undergoes only the dehydrogenation to diethyl ketone, the amount of diethyl ketone formed by the aldol route is given by

$$\begin{aligned} \text{DEK via the aldol route} &= \text{Moles of CO minus moles of 3-pentanol} \\ &= 0.123 - 0.004 \\ &= 0.119 \end{aligned}$$

The overall equations for the ester routes are



and



The equation (48) applies to the ester decomposition route involving the regeneration of n-propanol and the ester hydrolysis route involving the hydrolysis by water formed by the dehydration of n-propanol. The equation (55) applies to the ester hydrolysis route involving the hydrolysis by water formed by the dehydration of propionaldol.

One mole of carbon dioxide is formed per mole of the diethyl ketone formed by any of the ester routes. If it is assumed that carbon dioxide is formed by only reactions involved in the ester routes and does not react any further, the diethyl ketone formed by the ester routes is given by

$$\begin{aligned} \text{DEK via the ester routes} &= \text{moles of carbon dioxide formed} \\ &= 0.147 \\ \text{Total calculated DEK} &= 0.119 + 0.147 \\ &= 0.266 \end{aligned}$$

The calculated n-propanol is obtained by taking into

account the amounts of n-propanol corresponding to propionaldehyde, n-propanol, 3-pentanol, n-propyl propionate and 2-methyl-2-pentenal found in the reaction product and adding the amount of n-propanol corresponding to the diethyl ketone formed by the aldol route and the ester routes as calculated above. The diethyl ketone formed according to each of the equations (48) and (55) must be distinguished. This is done by assuming that the 2-methyl-2-pentenal formed does not react any further and that all the water formed by the dehydration of propionaldol is used in the hydrolysis of propyl propionate.

$$\text{DEK formed according to (55)} = 0.0142$$

$$\begin{aligned}\text{DEK formed according to (48)} &= 0.147 - 0.0142 \\ &= 0.1328\end{aligned}$$

$$\begin{aligned}\text{Calculated n-propanol} &= 1 \times 0.0972 + 1 \times 0.1510 + 2 \times 0.119 \\ &\quad + 3 \times 0.1328 + 4 \times 0.0142 + 2 \times \\ &\quad 0.0041 + 2 \times 0.0027 + 2 \times 0.0142 \\ &= 0.938\end{aligned}$$

The calculated hydrogen is also obtained by the procedure used for n-propanol and is given by

$$\begin{aligned}\text{Calculated hydrogen} &= 1 \times 0.0972 + 3 \times 0.1190 + 4 \times \\ &\quad 0.1328 + 6 \times 0.0142 + 2 \times 0.0041 \\ &\quad + 2 \times 0.0027 + 2 \times 0.0142 \\ &= 1.113\end{aligned}$$

Carbon balance obtained from the product distribution

$$\begin{aligned} &= 1/3(3 \times 0.0972 + 4 \times 0.0092 + 3 \times 0.1510 \\ &\quad + 5 \times 0.1430 + 6 \times 0.0112 + 5 \times 0.0041 \\ &\quad + 6 \times 0.0027 + 6 \times 0.0142 + 8 \times 0.0190 \\ &\quad + 0.123 + 0.147 + 3 \times 0.025) \\ &= 72.8\% \end{aligned}$$

The per cent liquid product retained by the chromatographic column is obtained by subtracting the per cent of the liquid product analysed by the column (Table XI) from 100.

APPENDIX V

GAS CHROMATOGRAMS AND INFRA-RED SPECTRA

1. Gas Chromatograms

The typical chromatograms obtained for the liquid and the gas products are shown in Figure 4, 5 and 6. The peaks corresponding to the identified products have been labelled. The relative retention times for all the components separated under conditions already described in the section on product identification are reported in the following table.

No.	Compound	Relative Retention Time
1	Air	-
2	Unknown	0.008
3	Unknown	0.029
4	Unknown	0.063
5	Unknown	0.088
6	Unknown	0.138
7	Unknown	0.163
8	Unknown	0.201
9	Propionaldehyde	0.255
10	Unknown	0.339
11	Unknown	0.381
12	Unknown	0.498
13	Methyl Ethyl Ketone	0.577

APPENDIX

TABLE 1. SUMMARY OF DATA FOR THE STUDY

TABLE 1. SUMMARY OF DATA FOR THE STUDY

The following table provides a summary of the data collected for the study. The data is organized into three main sections: General Information, Demographic Data, and Study Variables. Each section contains a list of variables and their corresponding values or descriptions. The data is presented in a clear and concise manner, allowing for easy comparison and analysis of the results.

Variable	Value	Variable	Value
Age	25.5	Gender	Male
Height	1.75	Weight	75.0
Weight	75.0	Body Mass Index	24.5
Body Mass Index	24.5	Heart Rate	72.0
Heart Rate	72.0	Blood Pressure	120/80
Blood Pressure	120/80	Cholesterol	180.0
Cholesterol	180.0	Glucose	90.0
Glucose	90.0	Insulin	10.0
Insulin	10.0	Hemoglobin A1c	5.7
Hemoglobin A1c	5.7	Diabetes	Yes
Diabetes	Yes	Medication	Insulin
Medication	Insulin	Dosage	10.0
Dosage	10.0	Frequency	Once daily
Frequency	Once daily	Duration	6 months
Duration	6 months	Follow-up	Yes
Follow-up	Yes	Compliance	High
Compliance	High	Adverse Effects	None
Adverse Effects	None	Overall Health	Good
Overall Health	Good	Quality of Life	High
Quality of Life	High	Satisfaction	High
Satisfaction	High	Recommendation	Yes
Recommendation	Yes	Study Status	Completed
Study Status	Completed	Final Report	Submitted
Final Report	Submitted	Publication	In Progress
Publication	In Progress	Archival	Yes
Archival	Yes	Access	Open
Access	Open	Version	1.0
Version	1.0	Update	None
Update	None	License	CC-BY
License	CC-BY	Copyright	2023
Copyright	2023	Author	John Doe
Author	John Doe	Editor	Jane Smith
Editor	Jane Smith	Reviewer	Dr. Alex Brown
Reviewer	Dr. Alex Brown	Editorial Board	Yes
Editorial Board	Yes	Peer Review	Yes
Peer Review	Yes	Journal	Journal of Health Research
Journal	Journal of Health Research	Volume	15
Volume	15	Issue	3
Issue	3	Page	123-135
Page	123-135	Word Count	5000
Word Count	5000	References	25
References	25	Tables	1
Tables	1	Figures	0
Figures	0	Supplements	0
Supplements	0	Appendices	1
Appendices	1	Index	1
Index	1	Glossary	1
Glossary	1	Abbreviations	1
Abbreviations	1	Acronyms	1
Acronyms	1	Footnotes	0
Footnotes	0	Endnotes	0
Endnotes	0	References	25
References	25	Tables	1
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Figures	0	Supplements	0
Supplements	0	Appendices	1
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Acronyms	1	Footnotes	0
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Endnotes	0	References	25
References	25	Tables	1
Tables	1	Figures	0
Figures	0	Supplements	0
Supplements			

No.	Compound	Relative Retention Time
14	Unknown	0.649
15	Unknown	0.849
16	n-Propanol	1.000
17	Diethyl Ketone	1.133
18	Ethyl Isopropyl Ketone	1.468
19	n-Propyl Propionate	1.737
20	3-Pentanol	1.828
21	2-Methyl-2-Pentenal	2.040
22	3-Octanone	2.145
23	Unknown	2.220
24	Unknown	2.455
25	Unknown	2.535
26	Unknown	2.870
27	Unknown	3.010
28	Unknown	3.120
29	Unknown	3.430
30	Unknown	3.770
31	Unknown	3.920

The relative retention times as reported above are the ratio of the time taken for the particular compound to elute with respect to that taken by n-propanol after allowing for the time taken for the air to elute.

3-Pentanol

n-Propyl Propionate

Ethyl Isopropyl
Ketone x2

Diethyl Ketone

x16

n-Propanol

Methyl x2
Ethyl
Ketone

Propionaldehyde

x2

Figure 4. Liquid Product Chromatogram

Sample injected

Attenuation is 1 except when marked otherwise

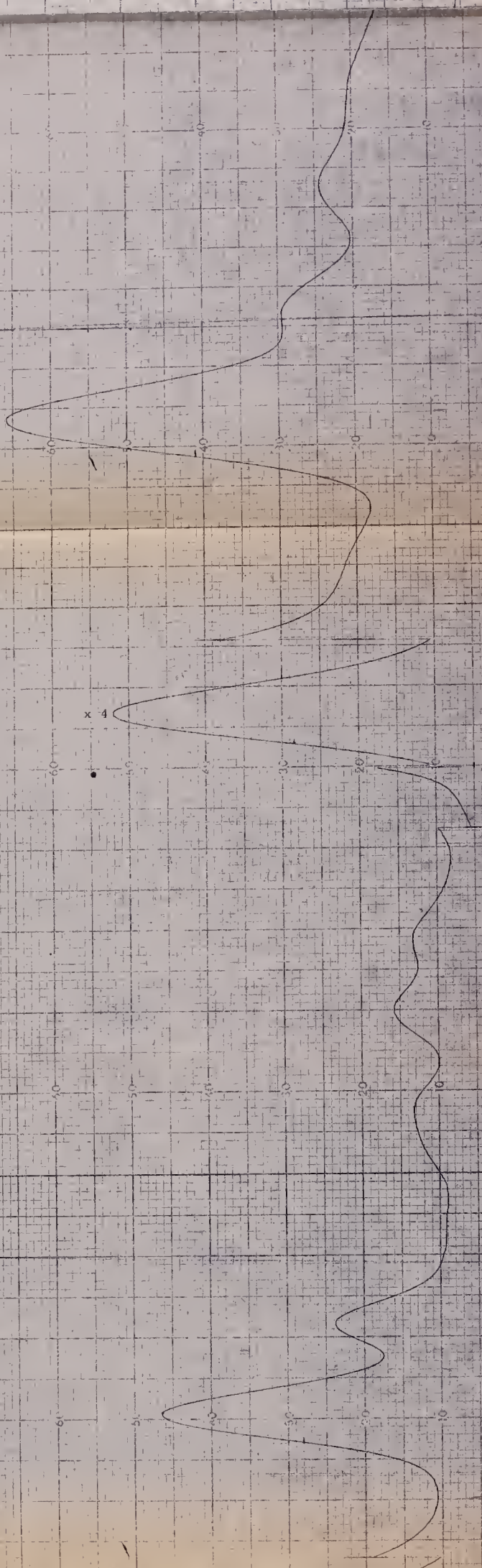
3-Octanone

x 4

2-Methyl-2-Pentenal

3-Pentanol

n-Propyl Propionate



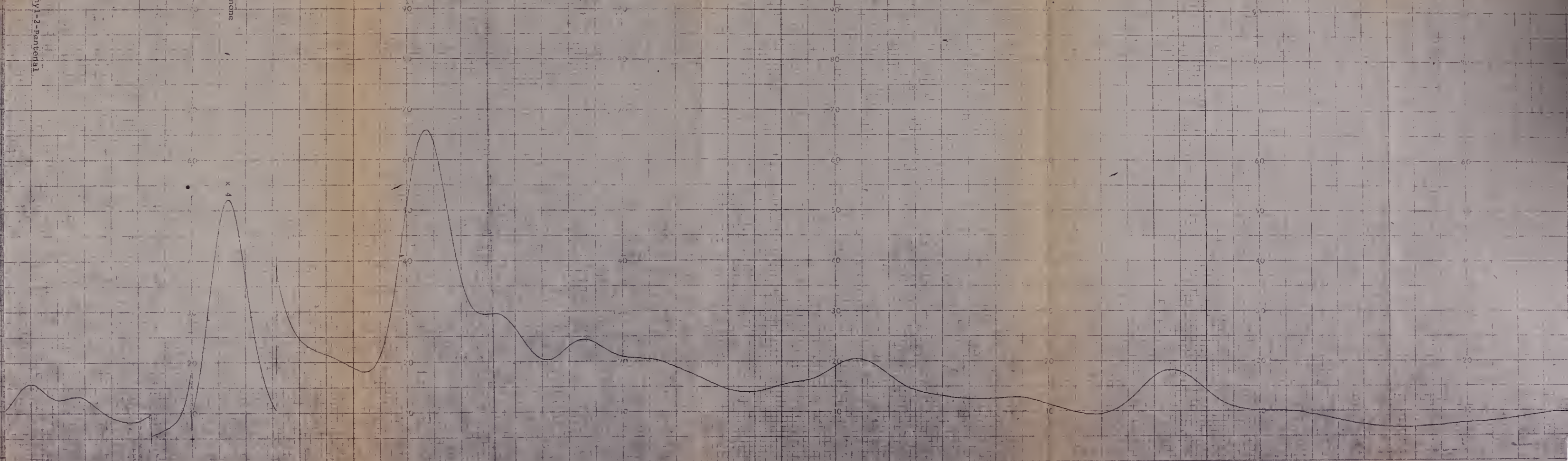
Sample injected

Attenuation is 1 except when marked otherwise

2-Methyl-2-Pentanol

3-Octanone

x 4



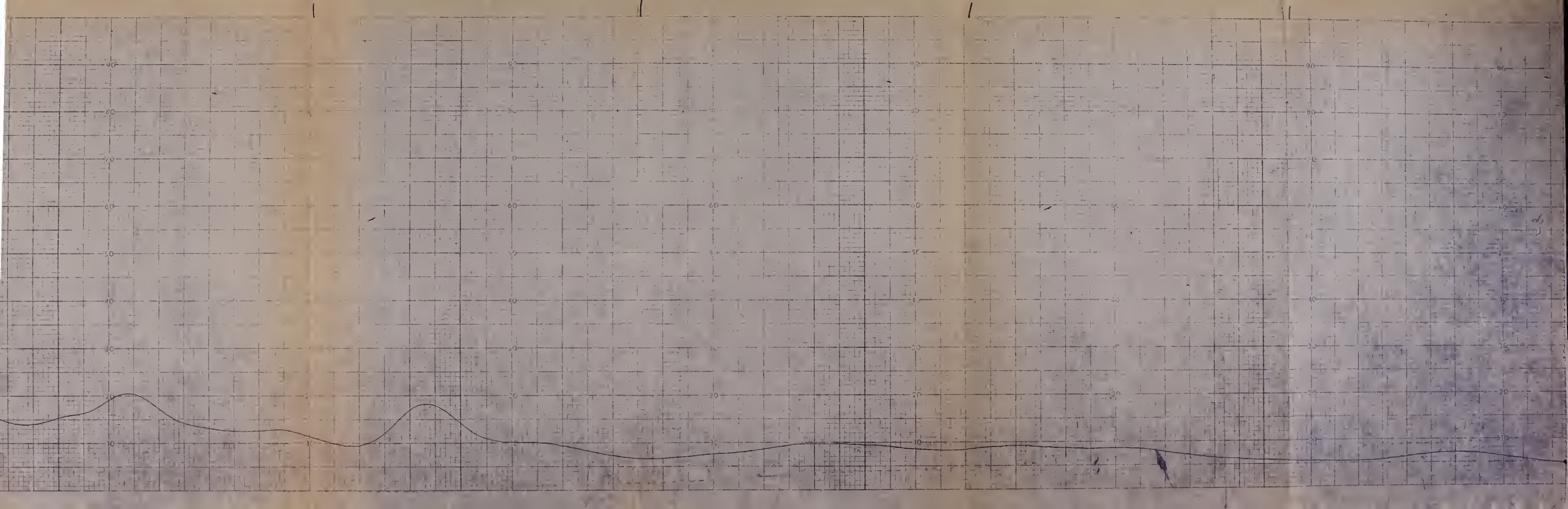


Figure 5. Gas Product Chromatogram 1

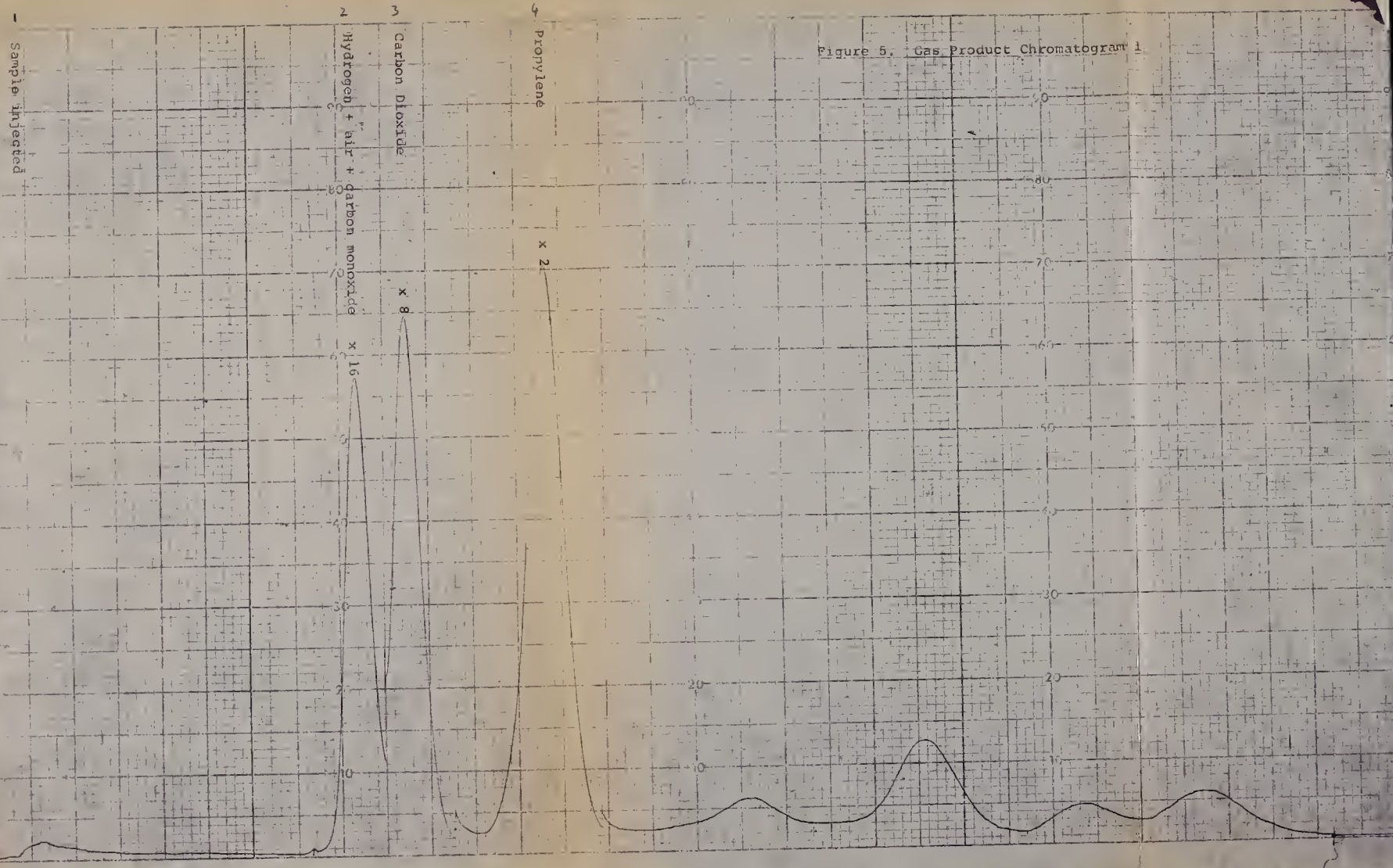
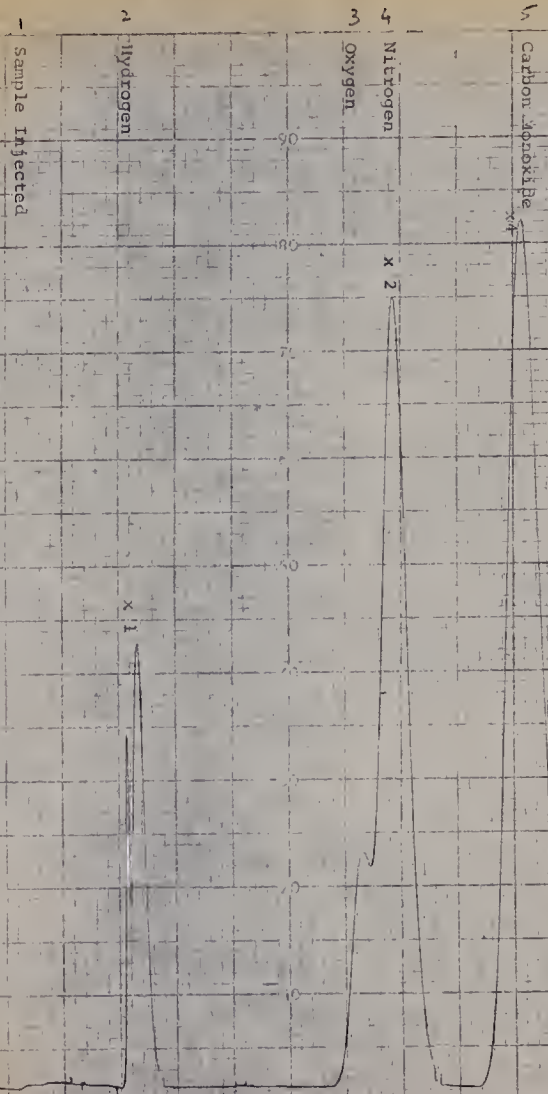


Figure 6. Gas Product Chromatogram II

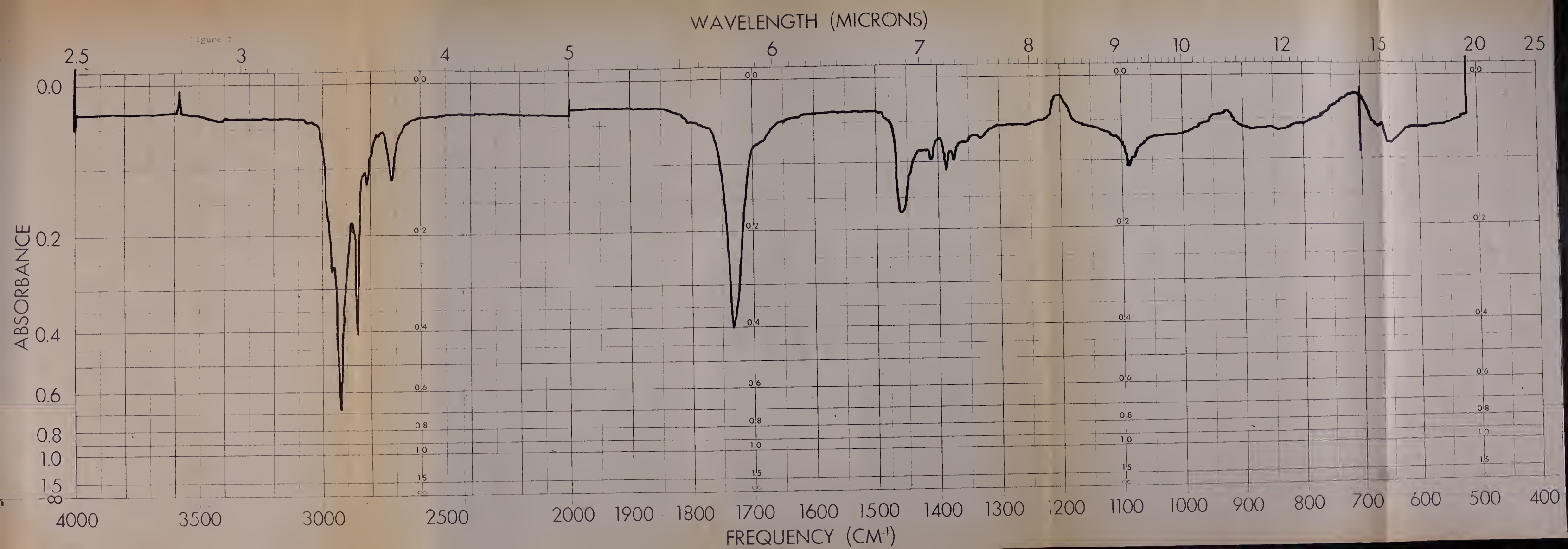


2. Infra-red Spectra

The infra-red spectra obtained for the components isolated by gas chromatography are reproduced in Figure 7 to 14. The chemical nature of each compound was established by interpretation of its infra-red spectrum. The chemical interpretations are listed along with the figure numbers in the following table:

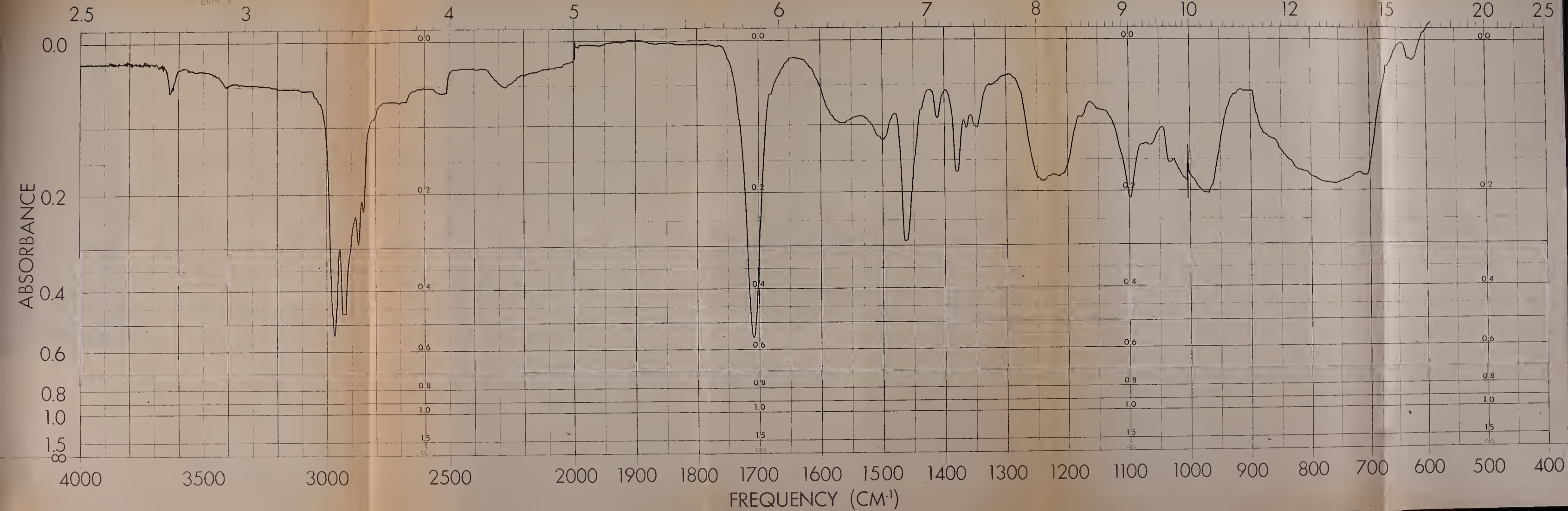
Figure	Nature of Compound
7	Saturated aliphatic aldehyde
8	Saturated open-chain ketone
9	Primary alcohol
10	Saturated open-chain ketone
11	Saturated open-chain ketone
12	Normal saturated ester
13	Unsaturated aldehyde
14	Saturated open-chain ketone

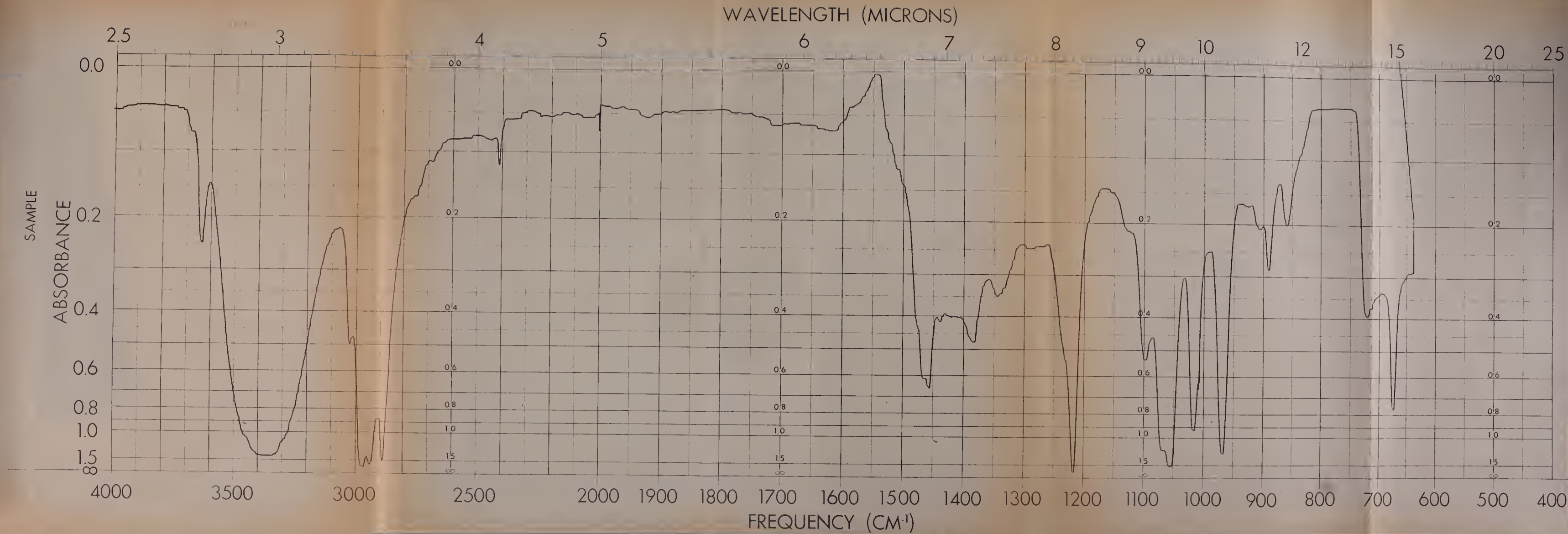
Figure 7

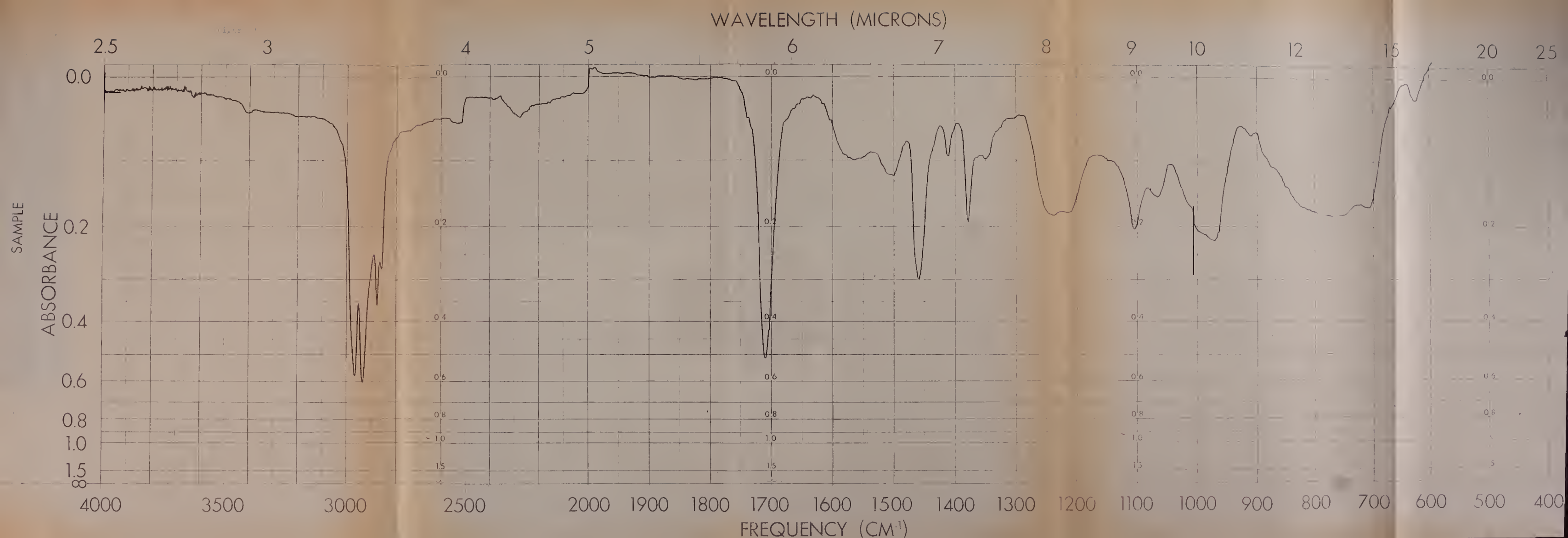


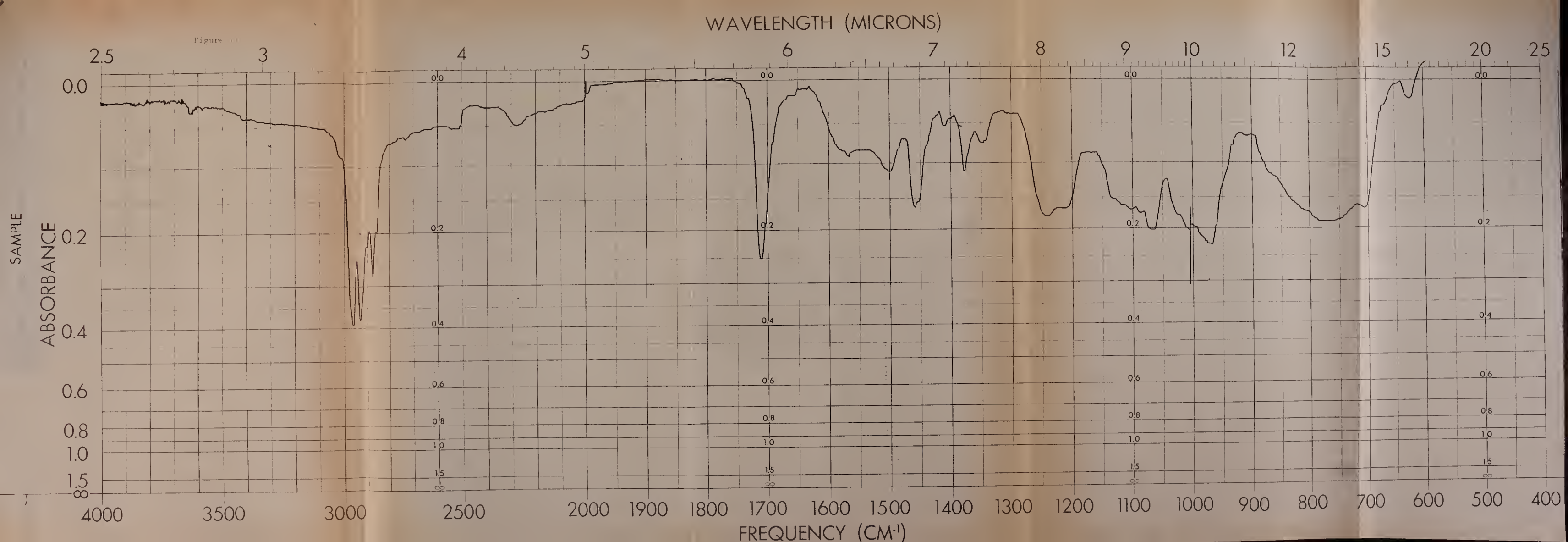
WAVELENGTH (MICRONS)

Figure 8

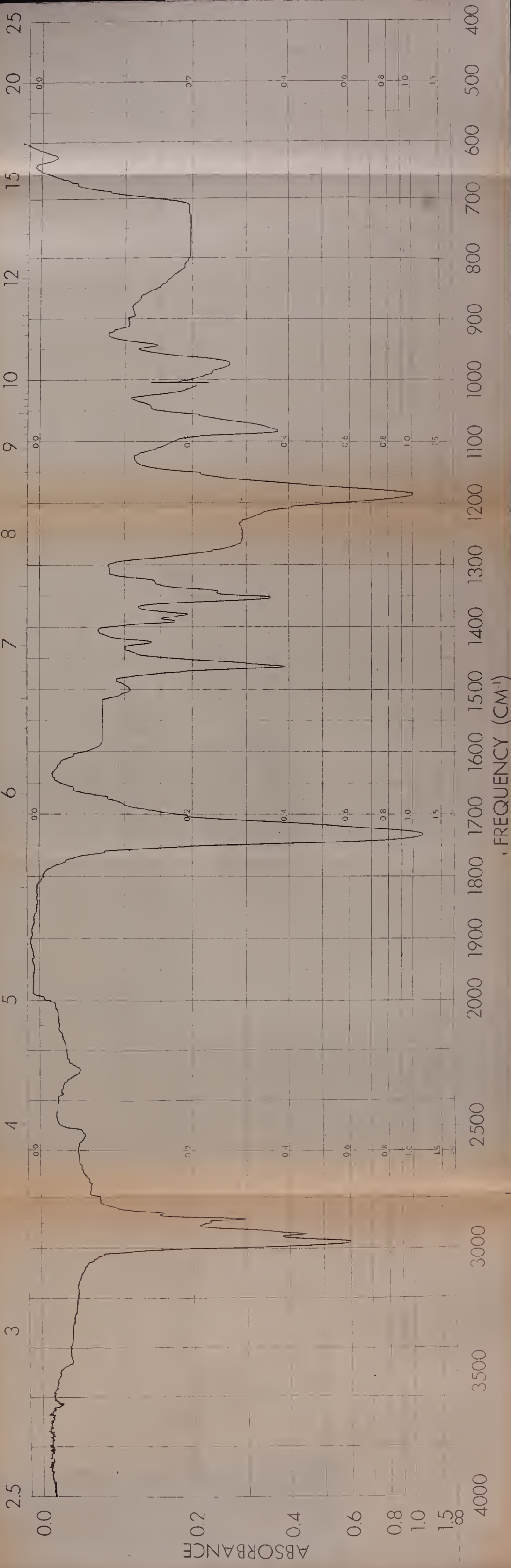








WAVELENGTH (MICRONS)

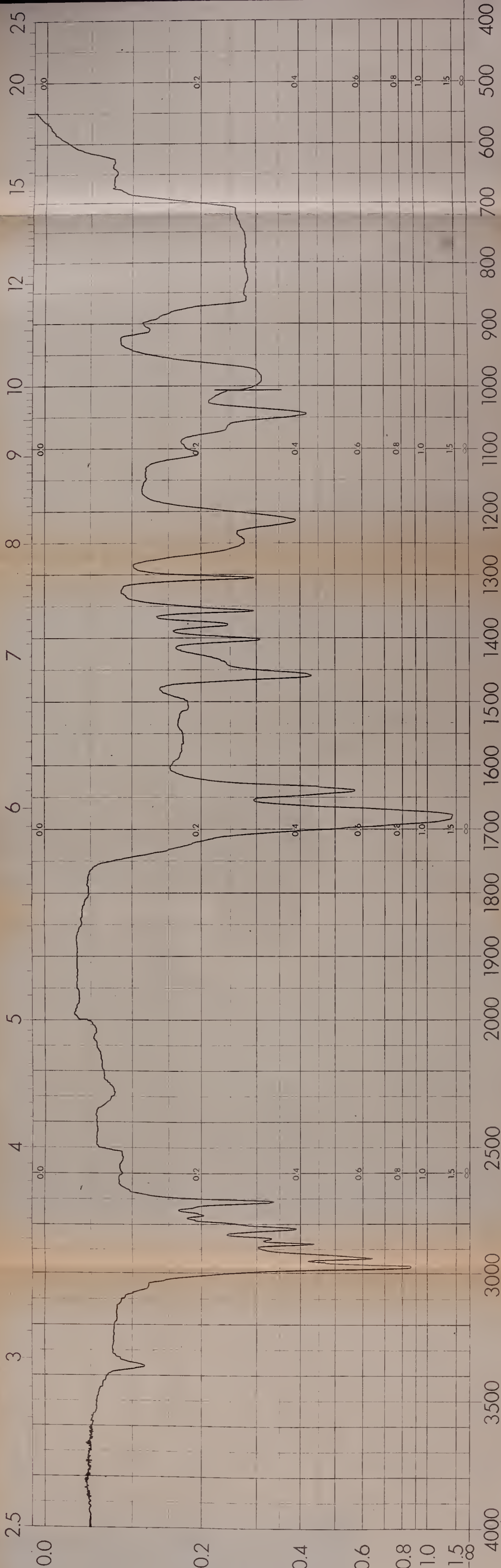


WAVELENGTH (MICRONS)

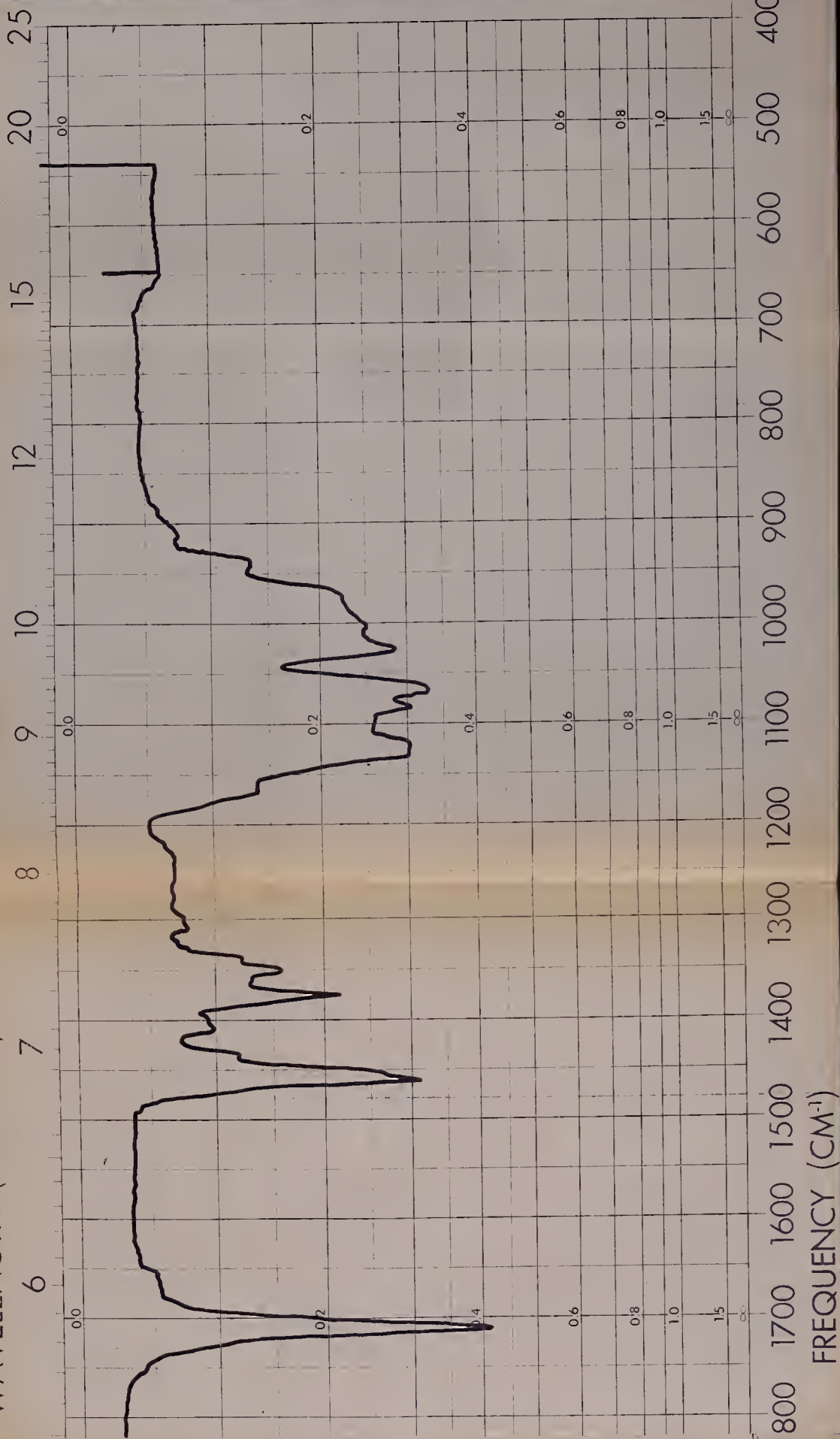
FREQUENCY (CM⁻¹)

SAMPLE

ABSORBANCE



WAVELENGTH (MICRONS)



SAMPLE

B29843